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16. ABSTRACT

The primary objective of this program was the development of methods for the analysis of priority pollutants in sludge. Independent methods were developed for purgeable and extractable compounds. For purgeables, a purge and trap-GC/MS procedure was developed utilizing a stirred bottom-frit chamber. Recoveries were comparable to the conventional purge tube without excessive foaming. A revised protocol developed for extractable priority pollutants employed homogenization/centrifugation extraction, GPC cleanup and GC/MS detection.

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DEVELOPMENT OF ANALYTICAL TEST PROCEDURES FOR THE MEASUREMENT OF ORGANIC PRIORITY POLLUTANTS IN SLUDGE

by

Clarence L. Haile
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Contract No. 68-03-2695
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Prepared for:

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory - Cincinnati, conducts research to:

- Develop and evaluate methods to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria and other microbiological organisms in water; and, to determine the responses of aquatic organisms to water quality.
- Develop and operate an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.
- Develop and operate a computerized system for instrument automation leading to improved data collection, analysis, and quality control.

Under authority of Sections 304(h) and 501(a) of the Federal Water Pollution Control Act of 1972 and the Clean Water Act of 1977, the Environmental Protection Agency is required to promulgate guidelines establishing test procedures for the analysis of pollutants. This report represents the state-of-the-art for the measurement of specific organic analytes in municipal and industrial sludge.

Robert L. Booth

Robert L. Booth, Acting Director
Environmental Monitoring and Support
Laboratory - Cincinnati

PREFACE

This is the final report for EPA Contract No. 68-03-2695, "Development of Analytical Test Procedures for the Measurement of Organic Priority Pollutants in Sludges and Sediments," conducted as Midwest Research Institute Project No. 4583-A. The project was directed by Dr. Clarence L. Haile. The work was performed in the Environmental Analysis Section, Dr. John E. Going, Section Head, under the supervision of Dr. James L. Spigarelli, Director of the Analytical Chemistry Department.

This report was written by Drs. Clarence L. Haile and Viorica Lopez-Avila. Technical support for the project was provided by Mrs. Alice Shan, Mr. Raymond V. Northcutt, Mr. Robert Goddard, Mr. Lee Malone, Mrs. Donna Rose, Mr. Richard Robson, Mr. Gil Radolovich, Mr. George Vaughn, Mr. Jon Onstot, and Ms. Margie Wickham.

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ABSTRACT

The primary objective of this research program was the development of methods for the analysis of organic priority pollutants in sludges generated from the treatment of municipal and industrial wastewaters. Independent methods were developed for the analysis of the extractable and purgeable organic priority pollutants.

Regarding the development of a method protocol for the extractables, the research program was conducted in two stages. In the first stage, a preliminary POTW sludge analysis protocol was developed from existing wastewater methods to satisfy U.S. Environmental Protection Agency (EPA) requirements for methods to be used in a survey of POTW wastewaters and sludges. Then, in the second stage, a systematic study of sludge analysis techniques was conducted, resulting in the development of a set of revised protocols.

A protocol for extractable compounds was developed based on the results of these method evaluations. The analytical scheme employed homogenization/centrifugation extraction, GPC cleanup and packed-column GC/MS for acidic extracts, and adsorption chromatographic cleanup and capillary column GC/MS for base/neutral extracts. GPC cleanup and packed-column GC/MS procedures were included as options for base/neutral extracts. The protocol was evaluated by analyzing aliquots of five primary sludges (three from POTW and two from industrial wastewater treatment plants) spiked with representative compounds at three levels. The precision and accuracy results indicated that these methods could be reliably applied to the analysis of acidic and base/neutral extractable compounds in sludge.

The method development study for purgeables was first directed toward applying and modifying the purge-and-trap gas chromatography/mass spectrometry (GC/MS) procedures specified by the U.S. Environmental Protection Agency (EPA) for industrial wastewater analyses. The wastewater method was adapted from the original purge and trap GC procedure for volatile compounds in water reported by Bellar and Lichtenberg.

In response to the need for a purgeables method for municipal sewage treatment sludges, a preliminary purge and trap GC/MS method was developed using sample dilution to control foaming. Preliminary experiments with sludges from publicly owned treatment works (POTW) indicated that most, but not all, sludges could successfully be purged if the sample aliquot was diluted to approximately 0.5% (w/v) total solids with 10-ml total volume. The recoveries for analytes spiked into POTW sludges and analyzed by this method are typical of those observed for high polluted wastewaters. Results of these studies often provided unacceptable precision values and the need for sample dilution increased the effective method detection limit. As a consequence, additional experiments were conducted. These studies were designed to develop a purging procedure with improved recoveries, reproducibility, and detection limits. The feasibility of using salt or organic additives to improve purging reproducibility was investigated and alternative purging systems incorporating mechanical mixing were evaluated to enhance analyte transfer to the purge gas stream.

As a consequence of these studies, a purge chamber, using a stirred bottom frit provided recoveries for compounds spiked into undiluted sludge and analyzed by purge and trap GC/MS that were as good as or better than the recoveries from dilution followed by purge and trap GC/MS with the conventional purge tube. The precision of recovery measurements was much better with the bottom frit tube, and no foaming problems were observed. In addition, analysis of undiluted 10-ml sludge aliquots provides a significant improvement in the method detection limit. Considering the variability of sludge characteristics, the heterogeneous nature of sludges and the detection limits achieved, the results of these precision and accuracy determinations demonstrate that the proposed method can reliably be applied to the analysis of purgeable compounds in municipal and industrial wastewater treatment sludges.

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SECTION 1

SUMMARY

The primary objective of this research program was to develop methods for the analysis of organic priority pollutants in sludges generated from the treatment of municipal and industrial wastewaters. Historically, studies of emissions from wastewater treatment plants have focused on determining the concentrations of contaminants in influent and effluent wastewaters and on their removal as the wastewater passed through the treatment system. Since many of the organic priority pollutants have very low solubilities in water, significant portions of these compounds are likely associated with suspended solids. Hence, sludge wasting may be a primary emission mode for organic priority pollutants.

This research program was conducted in four stages. In the first stage, a preliminary protocol was developed from existing wastewater methods to satisfy immediate Environmental Protection Agency (EPA) requirements for methods to be used in a survey of publicly owned treatment works (POTW) wastewaters and sludges. Then, in the second stage, a systematic study of sludge analysis techniques was conducted, resulting in the development of a set of revised protocols for municipal and industrial sludges. The third stage was an evaluation of the precision and accuracy of the revised protocols. The revised methods were used in the fourth stage to determine the distribution of compounds in sludge between the supernatant and solids. In addition, a brief study of the applicability of the sludge methods for sediment analysis was conducted.

To expedite the development of workable preliminary methods for POTW sludge, the primary approach was to adapt and evaluate the current EPA methods for screening industrial wastewaters for organic priority pollutants. Following the scheme of the industrial wastewater methods, the compounds were analyzed in three fractions: purgeables, basic and neutral extractables, and acidic extractables. The purge-trap gas chromatographic/mass spectrometric (GC/MS) method for purgeable compounds in wastewaters was modified for sludges by simply diluting the sludge to approximately 0.5% (weight/volume) suspended solids prior to purging. The dilution was necessary to decrease the incidence of excessive foaming. This preliminary method provided fairly good recoveries for representative purgeable compounds but the precision was poor. In addition, sample dilution increased the method detection limit.

Development of a revised method for purgeables focused on improving both the method precision and recoveries for spiked compounds. The results of recovery experiments for compounds spiked into sludge and supernatant from centrifuged sludge indicated that dissolved solids had little effect on purging efficiencies. Subsequent experiments investigated the feasibility of using

salt or a nonvolatile organic (ethylene glycol) in the dilution water to mitigate the effects of suspended solids on purging efficiencies and reproducibility. The results of these experiments, although confirming that dissolved solids did not appreciably affect purging, demonstrated that additives did not improve the performance of the purging system. Further experiments were directed to evaluating of alternate purging hardware that provided mechanical mixing of the sludge during purging.

The results of preliminary evaluations of stirred purging and stirred dynamic headspace systems configured with a small round-bottom flask and tested with spiked water indicated that neither system was as efficient as the conventional purge tube which had been used in the preliminary method. A new purge tube was designed by adapting the conventional purge tube to allow for the use of a magnetic stirrer. The diameter of the tube was enlarged to increase the exposed sample surface area and to reduce the potential for sample foaming. In practice, the combination of tube geometry and stirring effectively retarded foaming so that even 10-ml aliquots of undiluted sludge were purged without appreciable foaming. This stirred bottom frit tube provided recoveries for spiked compounds that were as good as or better than the recoveries from the preliminary method but with much better reproducibility. In addition, purging 10-ml aliquots of undiluted sludge provided significantly better detection limits. Hence, this bottom frit purge tube was included in a revised purge-trap GC/MS method for sludge.

Adapting the EPA wastewater screening methods for extractable organic priority pollutants in sludges involved the development of sample extraction and extract cleanup procedures to produce extracts suitable for GC/MS analysis. A homogenization/centrifugation extraction method was used with gel permeation chromatographic (GPC) cleanup in the preliminary POTW sludge protocol. Although these methods provided fairly good recoveries for the basic, neutral, and acidic compounds, the extraction procedure was labor-intensive and time-consuming. Hence, the development of revised methods for industrial and municipal wastewater treatment sludges focused on more efficient and simpler extraction methods and extract cleanup procedures appropriate for the selected extraction method. The alternate extraction methods evaluated were continuous liquid-liquid extraction, extractive steam distillation, and microextraction. The continuous liquid-liquid extraction procedure was ineffective for extracting compounds that tend to strongly associate with suspended solids. Extractive steam distillation did not provide good recoveries for compounds with low volatilities. Although microextraction has been successfully used for rapid and simple extraction of wastewaters, recovery of the extracts from sludge was difficult. Hence, only the homogenization/centrifugation extraction procedure provided good recoveries for the entire range of extractable compounds.

Since the homogenization/centrifugation procedure was not very selective, further development of extract cleanup procedures was conducted. Several alternate GPC systems, i.e., combinations of eluting solvent and resins, were evaluated. The best overall performance was achieved with the system used in the preliminary POTW sludge protocol, Bio-Beads SX-3 eluted with dichloromethane. In addition to the GPC procedures, two essentially equivalent adsorption chromatographic cleanup procedures using silica gel and florisil were developed. These procedures were applicable only to the base/neutral compounds, since the phenols were not separated from the polar interferences. Although the silica gel and florisil procedures provided generally cleaner extracts than GPC, the GPC method can be automated to require much less labor. An adsorption chromatographic method using cesium silicate was evaluated for the acid compounds. However, the method recoveries were good when only moderate or low levels of coextractants were present.

A capillary GC/MS method was developed for the base/neutral compounds to improve analysis of complex extracts. Of the four wall-coated open tubular columns evaluated, the fused silica column coated with SE-54 provided the best resolution and inactivity.

A revised protocol for extractable compounds was developed based on the results of these method evaluations. The analytical scheme employed homogenization/centrifugation extraction, GPC cleanup, and packed column GC/MS for acidic extracts and adsorption chromatographic cleanup and capillary column GC/MS for base/neutral extracts. GPC cleanup and packed column GC/MS procedures were included as options for base/neutral extracts.

The revised protocols for purgeables and extractables were evaluated by analyzing aliquots of five primary sludges (three from POTWs and two from industrial wastewater treatment plants). All were spiked with representative compounds at three levels. The precision and accuracy results indicated that these methods could be reliably applied to the analysis of purgeable and acidic and base/neutral extractable compounds in sludge.

The distributions of representative compounds spiked into 1% primary sludge were determined using the revised protocols for purgeables and extractables. Distribution coefficients were calculated from the concentrations measured in supernatants and solids for two POTW sludges spiked at two or more levels.

The preliminary purgeables and extractables methods were evaluated for their applicability to sediment analysis. Although the purging and extraction procedures had to be modified somewhat for sediments, both methods provided fairly good recoveries for representative compounds spiked into three river sediments.

SECTION 2

RECOMMENDATIONS

1. Evaluate the performance of the protocols for all organic priority pollutants. The method evaluation experiments described in this report were conducted only on a subset of the organic priority pollutants which had been selected to represent chemical and physical properties of the entire set. Hence, the precision and accuracy of the protocols should be evaluated for the entire set of compounds.

2. Develop additional methods for specific problem compounds. Although the protocols developed in this program were designed to be applicable to the entire set of organic priority pollutants, the methods were not entirely successful for all compounds. Additional methods development should be focused on specific compound classes, e.g., the benzidines, chloroalkyl ethers, and nitrosamines, for which the protocols were ineffective.

3. Develop additional internal standard and surrogate spiking compounds. Much of the variability inherent in trace analyses in difficult samples can be decreased through the use of internal standard compounds. Surrogate spiking compounds can provide recovery information for each sample analyzed without increasing the number of replicates analyzed. A repository of priority pollutant internal standard and surrogate spiking compounds should be established. Since the compounds must be very similar to the analytes, nonreactive stable isotope labeled compounds, e.g., ^{13}C and ^{37}Cl compounds, are the most appropriate choices.

4. Determine acceptable sample storage times and develop preservation techniques to maintain sludge sample integrity. The stability of the organic priority pollutants in sludge should be determined for a variety of sludges and analytes, and storage and preservation guidelines should be established.

5. Develop additional capillary GC/MS methods. Although capillary GC/MS may not be necessary for analysis of all samples, the better efficiency and resolution provided by capillary columns are extremely useful for analysis of very complex extracts. In addition to the methods described in this report for base/neutral compounds, capillary methods should be developed for acids, using columns which are less susceptible to rapid performance degradation. Capillary methods for purgeables would be helpful for some samples.

6. Evaluate the performance of these methods for each new medium to which it is to be applied. The methods described in this report were developed for application to wastewater treatment sludge only. They must be reevaluated for their applicability to other media such as soil, sediment, and sludges unrelated to wastewater treatment.

7. Expand the phase distribution data set. The phase distribution experiments described resulted in limited distribution information for several compounds. However, the number of data points throughout the concentration range of the experiments for each compound was not sufficient to accurately determine relationships between distribution and concentraton. Additional experiments should focus on obtaining data to accurately define these relationships for a few compounds and then to address additional compounds.

SECTION 3

INTRODUCTION

The primary objective of this research program was to develop methods for the analysis of organic priority pollutants in sludges generated from the treatment of municipal and industrial wastewaters. Historically, studies of emissions from wastewater treatment plants have focused on determining the concentrations of contaminants in influent and effluent wastewaters and on their removal as the wastewater passed through the treatment system. Likely contaminant removal mechanisms include volatilization, chemical and/or biochemical degradation, and removal on solids via sedimentation. Many of the organic priority pollutants have very low solubilities in water. Hence, it is likely that a significant fraction of these compounds are associated with the solids removed from the influent wastewater by primary sedimentation or become associated with solids formed during secondary and tertiary wastewater treatment (which are removed from the effluent wastewater by sedimentation). Since solids removal is an important part of wastewater treatment and the solids are likely carriers of hydrophobic contaminants, sludge wasting may be a primary emission mode for organic priority pollutants.

Although the term sludge is applied to any high solids effluent from wastewater treatment, the characteristics of sludges are very diverse. Sludges generally contain high levels of both dissolved and suspended organics. Sludges from publicly owned treatment works (POTW), i.e., municipal sewage treatment plants, and industrial wastewater treatment plants receiving wastes of biological origin, e.g., process wastewaters from leather tanning, typically contain high levels of high molecular weight organics related to humic materials. Most of the organics in sludges from the treatment of synthetic organic process wastewaters have lower molecular weights. These sludges tend to have lower solids content than POTW sludges. The characteristics of sludges also differ according to their origin within the treatment process. Primary sludges (from simple sedimentation) typically contain higher suspended solids levels and more dissolved organics than do secondary sludges (from sedimentation following biological treatment). The solids in sludges from tertiary treatment processes may be primarily inorganic salts formed from the chemical treatment additives. In addition, treatment of raw sludges by anaerobic or aerobic digestion or other processes practiced at some facilities alters the nature of the sludge finally wasted. This tremendous diversity of sludge characteristics, coupled with the heterogeneous nature of sludges, presents a considerable challenge to precise and accurate determinations of trace levels of the organic priority pollutants in sludges.

This research program was conducted in four stages. In the first stage, a preliminary POTW sludge analysis protocol was developed from existing wastewater methods to satisfy immediate Environmental Protection Agency (EPA) requirements for methods to be used in a survey of POTW wastewaters and sludges. To expedite development of a workable method, the primary research approach was to evaluate and adapt the EPA protocol for screening industrial wastewaters[1] for use with sludges. Following the scheme of the industrial wastewater methods, the compounds were to be analyzed in three fractions: purgeables, basic and neutral extractables, and acidic extractables. Then, in the second stage, a systematic study of sludge analysis techniques was conducted, resulting in the development of a set of revised protocols. The third stage was an evaluation of the precision and accuracy of the revised protocols. The revised methods were used in the fourth stage to determine the distribution of compounds in sludge between the supernatant and solids. In addition, a brief study of the applicability of the sludge methods for sediment analysis was conducted.

The method development and evaluation experiments described in this report were conducted using a subset of the organic priority pollutants to simplify sample spiking and recovery determinations. These compounds were selected by EPA to represent the physical and chemical characteristics of most of the organic priority pollutants. The list of spiking compounds is shown in Table 1. In general, these compounds were used in all experiments except in a few instances in which some compounds were temporarily unavailable.

The development and evaluation of the preliminary and revised methods for purgeable and extractable compounds were described in Sections 4 and 5 of this report. Section 6 presents the results of an evaluation of the applicability of the preliminary methods for organic priority pollutants analyses of sediments. The final section describes the results of determinations of the distribution of selected purgeable and extractable compounds in 1% sludges. The revised method protocols for both purgeables and extractable compounds are contained in a Method Appendix.

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[1] U. S. Environmental Protection Agency. Sampling and Analysis Procedures for Screening of industrial Effluents for Priority Pollutants. Environmental Monitoring and Support Laboratory, Cincinnati, Ohio. Revised April 1977.

TABLE 1. REPRESENTATIVE ORGANIC PRIORITY POLLUTANTS USED FOR METHOD DEVELOPMENT AND EVALUATION EXPERIMENTS

Purgeable Compounds

- Benzene
- Carbon tetrachloride
- Chlorobenzene
- Chloroform
- 1,2-Dichloroethane
- 1,1-Dichloroethane
- Ethylbenzene
- Tetrachloroethane
- 1,1,1-Trichloroethane
- Trichloroethane
- Vinyl chloride

Extractable Compounds

- Acenaphthylene
- Benzidine
- Benzo[a]pyrene
- Bis(2-chloroethyl)ether
- Bis(2-chloroisopropyl)ether
- Bis(2-ethylhexyl)phthalate
- Butylbenzylphthalate
- 3,3'-Dichlorobenzidine
- 2,4-Dichlorophenol
- 2,4-Dimethylphenol
- 2,6-Dinitrotoluene
- Fluoranthene
- Hexachloroethane
- N-Nitrosodimethylamine
- 1,4-Dichlorobenzene
- Pentachlorophenol
- Phenol

SECTION 4

DEVELOPMENT AND EVALUATION OF METHODS FOR PURGEABLE COMPOUNDS

The development of methods for the analysis of volatile compounds in sludge was primarily directed toward applying and modifying the purge-trap gas chromatography/mass spectrometry (GC/MS) procedure specified by EPA for industrial and wastewater analyses.[1] The wastewater method was adapted from the original purge-trap GC procedure for volatile compounds in water reported by Bellar and Lichtenberg.[2] Volatile compounds that are sparingly soluble in water are sparged from a 5-ml aliquot of water with an inert gas stream. The analytes are adsorbed from the gas stream by a trap containing Tenax GC® and silica gel. The adsorbed compounds are then thermally desorbed into the inlet of a gas chromatograph interfaced with a mass spectrometer. Schematics of the purge-trap system in the sparge (or purge) and desorb modes are shown in Figures 1 and 2. The Tenax-silica gel trap used for industrial wastewater was modified as suggested later by T. A. Bellar[3] to improve adsorption of the very volatile fluorochloromethanes. The packing of this trap is shown in Figure 3. The sample purging tube used by MRI for wastewater is shown in Figure 4. The tube is a chromatographic column with a medium porosity frit pressed into the polytetrafluoroethylene (TFE) stopcock assembly.

The suitability and performance of the trapping, desorption, and GC/MS determination segments of the purge-trap GC/MS method have been demonstrated for a variety of difficult wastewaters and other aqueous samples. Hence, the primary objective of this work was to adapt the purging system for sludge. Organic surfactants are frequently contained within the heterogeneous suspension of sludges. As a result, sludge aliquots tend to generate copious quantities of foam during purging. Although some foaming may be controlled by placing a plug of precleaned glass wool in the top of the purge tube or through the use of other mechanical foam traps, these measures are frequently ineffective when purging sludge aliquots. Excessive foaming can potentially reach the trap and saturate the silica gel, necessitating replacing the trap and thoroughly cleaning the system.

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[2] Bellar, T. A. and J. J. Lichtenberg. Determining Volatile Organics at Microgram-per-Liter Levels by Gas Chromatography. JAWWA 66:739-744 (1974).

[3] Bellar, T. A. Environmental Monitoring and Support Laboratory, Environmental Protection Agency, Cincinnati, personal communication (1978).

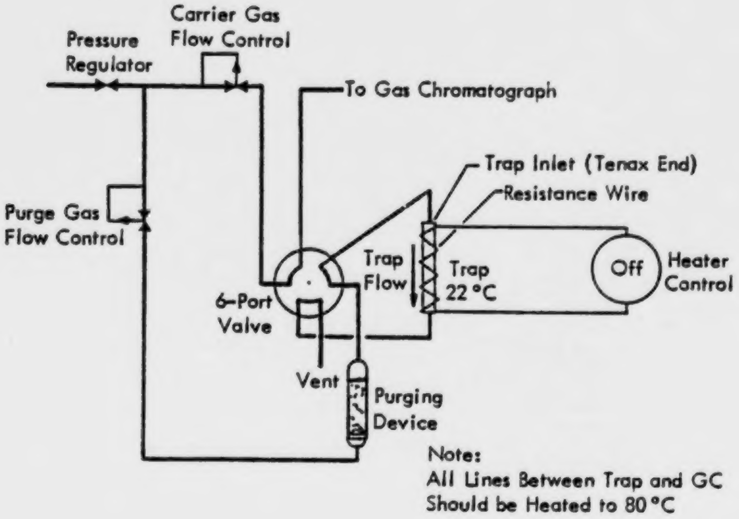
Carrier Gas
Flow Control
Pressure
Regulator
To Gas Chromatograph
Trap Inlet (Tenax End)
Resistance Wire
Purge Gas
Flow Control
Trap
Flow
Trap
22 °C
Off
Heater
Control
6-Port
Valve
Vent
Purging
Device
Note:
All Lines Between Trap and GC
Should be Heated to 80 °C

Figure 1. Schematic of the purge-trap system in the purge mode.

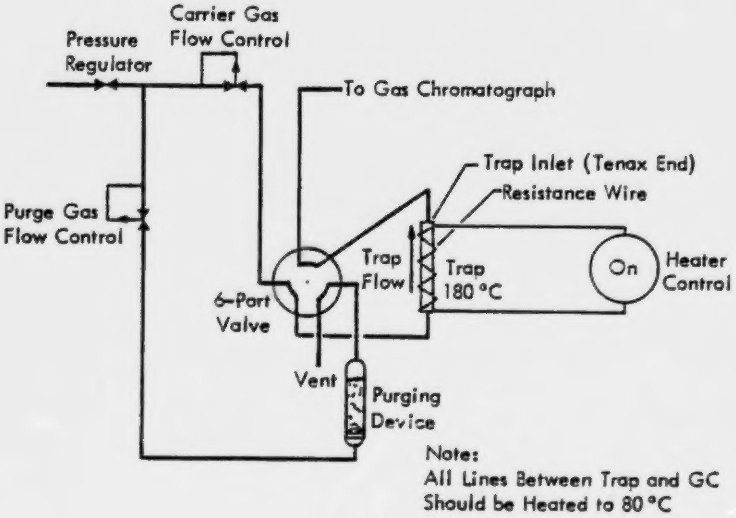
Carrier Gas
Flow Control
Pressure
Regulator
To Gas Chromatograph
Trap Inlet (Tenax End)
Resistance Wire
Purge Gas
Flow Control
Trap
Flow
Trap
180 °C
On
Heater
Control
6-Port
Valve
Vent
Purging
Device
Note:
All Lines Between Trap and GC
Should be Heated to 80 °C

Figure 2. Schematic of the purge-trap system in the desorb mode.

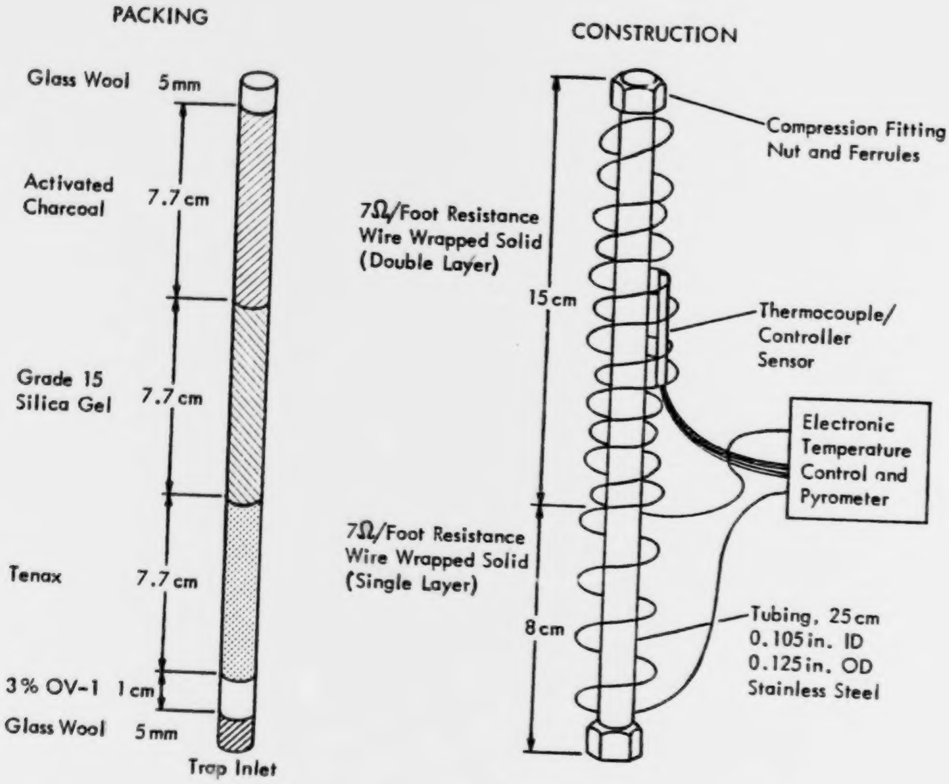
PACKING
Glass Wool 5 mm
Activated Charcoal 7.7 cm
Grade 15 Silica Gel 7.7 cm
Tenax 7.7 cm
3% OV-1 1 cm
Glass Wool 5 mm
Trap Inlet
CONSTRUCTION
Compression Fitting Nut and Ferrules
7Ω/Foot Resistance Wire Wrapped Solid (Double Layer)
15 cm
Thermocouple/ Controller Sensor
Electronic Temperature Control and Pyrometer
7Ω/Foot Resistance Wire Wrapped Solid (Single Layer)
8 cm
Tubing, 25 cm 0.105 in. ID 0.125 in. OD Stainless Steel

Figure 3. Trap packings and construction.

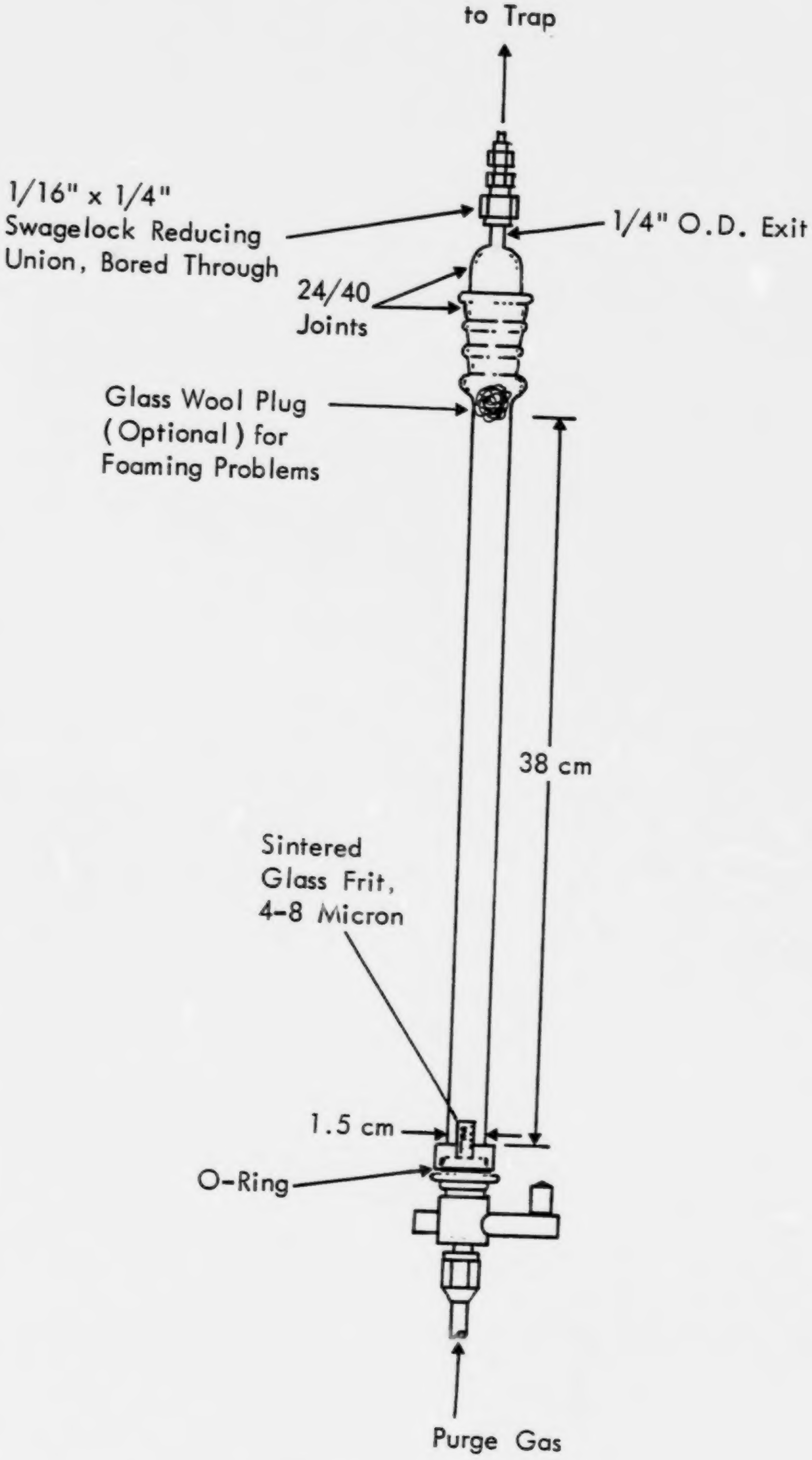
to Trap
1/16" x 1/4" Swagelock Reducing Union, Bored Through
1/4" O.D. Exit
24/40 Joints
Glass Wool Plug (Optional) for Foaming Problems
38 cm
Sintered Glass Frit, 4-8 Micron
1.5 cm
O-Ring
Purge Gas

Figure 4. Purging tube.

In response to an expressed immediate EPA need for a purgeables method for POTW sludge, relatively simple solutions to the foaming problem were evaluated. Following development of the preliminary method for POTW sludge, more basic experiments were conducted to develop a more efficient sludge purging system. At the conclusion of these experiments, a revised protocol for purgeable compounds in sludge was designed. The precision and accuracy of the revised procedure were evaluated in five samples of POTW and industrial primary sludge, and the labor- and instrument-hours required for conducting analyses with this protocol were estimated.

DEVELOPMENT OF A PRELIMINARY PROTOCOL FOR POTW SLUDGE

Two relatively expedient solutions to the foaming problem are to (a) use antifoam additives or (b) dilute the sample. Dilution was selected to decrease the potential for adversely altering the purging characteristics of the analytes and for introducing contaminants. Dilution does, however, decrease the effective method detection limit. Preliminary experiments indicated that most sludges could be successfully purged if the sample aliquot was diluted to approximately 0.5% suspended solids (weight/volume) with a 10-ml total volume. For example, a 2.0-ml aliquot of sludge containing 5% suspended solids was diluted to 10 ml prior to purging. Following this dilution, the sludge aliquot was purged and analyzed in the same manner as a wastewater aliquot. This purge-trap GC/MS method was evaluated for sludges as described below.

Experimental

A sample of primary sludge was obtained from the Platte County sewage treatment plant (Kansas City, Missouri). Samples of combined and aerobically digested sludge were taken from the Little Blue River sewage treatment plant (Independence, Missouri). The suspended solids contents of each sample were determined gravimetrically for 1.0-ml aliquots dried overnight at 110°C. Five 25-ml screw-cap vials, each containing three stainless steel balls (3.2 mm or 1/8 in. diameter), were filled with each sludge sample. Three individual vials for each sample were spiked with the purgeable spiking compounds dissolved in 5 to 10 µl of methanol. All vials were sealed with TFE-lined septa and were allowed to equilibrate at 4°C overnight, with tumbling, prior to analysis.

Duplicate unspiked aliquots and triplicate aliquots of each sludge type were analyzed as follows. Depending on the solids content of the sample, a 2.0- to 5.0-ml aliquot of the sludge was transfered to the purge tube and diluted to 10 ml. The diluted sludge aliquot was spiked with 9 µl of an internal standard spiking solution containing 20 ng/µl each of bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane in organic-free water. The purge tube was then sealed into the purging system. The sludge was purged with prepurified nitrogen for 12 min at 40 ml/min. Following purging, the trap was rapidly heated to 180°C to thermally desorb the volatiles into the inlet of the gas chromatograph. The desorption condition, with the trap at 180°C, was maintained for 3 min. The column temperature program was initiated at the same time desorption was started. The GC column (2.4 m x 2 mm ID glass, packed with 0.2% Carbowax 1500 on 60/80 mesh Carbopack C) was held at

40°C for 3 min, programmed to 170°C at 10°C/min, and then maintained at 170°C until after the elution time for ethylbenzene. The mass spectrometer was repetitively scanned over the range m/e 20-275 at 5 s/scan.

The analytes were identified by the coincidence of peaks in extracted ion current plots (EICP) plotted for characteristic ions at the appropriate retention time and in the characteristic relative intensity ratios as described in the industrial wastewater screening protocol.[1] The analytes were quantitated by comparing the height of the EICP peaks with those for mixed standards spiked into volatiles-free water and analyzed in the same manner as the diluted sludge aliquots. Concentrations of analytes were calculated using internal standard correction as follows:

$$\left(\frac{A}{B}\right)\left(\frac{B_{IS}}{A_{IS}}\right)\left(\frac{N}{V}\right) = \mu g/\text{liter of sludge}$$

where:

A = height of peak in sample

B = height of peak in standard

A_{IS} = height of internal standard peak in sample

B_{IS} = height of internal standard peak in standard

N = nanograms in standard

V = volume of sludge analyzed (ml)

The first run for each analysis day was a system blank consisting of a 10-ml aliquot of volatiles-free water spiked with the internal standard solution.

Results and Discussion

The results of the recovery experiments with spiked primary, combined, and aerobically digested sludge (solids contents of 2.0, 1.0, and 2.5%, respectively) are summarized in Table 2. With the exception of carbon tetrachloride from the combined sludge, all compounds were recovered from all three sludges. However, the recoveries were somewhat variable. The mean relative standard deviations of the recoveries for all compounds for the primary, combined, and digested sludge were 41, 46, and 51%, respectively. Part of this variability may be attributable to an inability to select a truly representative aliquot of a heterogeneous sample. Several compound recoveries were likely perturbated by the presence of high concentrations of those compounds in the unspiked sludge. In general, recoveries were fairly good for compounds that are easily recovered from wastewaters and were poor for compounds difficult to recover

TABLE 2. RESULTS OF EVALUATION OF PURGEABLES METHOD FOR POTW SLUDGES

Compound	Spike[a] (ng)	Primary sludge Unfortified[b] (ng)	Primary sludge Recovery (%)	Combined sludge Unfortified[b] (ng)	Combined sludge Recovery (%)	Digested sludge Unfortified[b] (ng)	Digested sludge Recovery (%)
Benzene	250	12	110 ± 8[c]	22	74 ± 26	600	27 ± 4
Carbon tetrachloride	250	ND[d]	92 ± 18	ND	0	ND	69 ± 6
Chlorobenzene	250	ND	65 ± 18	ND	85 ± 23	52	120 ± 4
Chloroform	250	29	97 ± 62	ND	120 ± 64	38	82 ± 47
1,2-Dichloroethane	250	ND	37 ± 26	ND	25 ± 9	ND	62 ± 28
1,1-Dichloroethene	250	11	110 ± 43	11	64 ± 46	48	76 ± 46
Ethylbenzene	250	ND	92 ± 22	ND	89 ± 30	110	110 ± 72
Tetrachloroethene	250	38	120 ± 32	56	94 ± 66	160	12 ± 21
1,1,1-Trichloroethane	250	98	120 ± 21	100	94 ± 41	29	64 ± 52
Trichloroethene	250	79	58 ± 41	16	94 ± 42	36	61 ± 16
Vinyl chloride	250	160	72 ± 60	e	120 ± 57	38	60 ± 14

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[a] The spiking concentrations were chosen so that the aliquots analyzed (2-5 ml) contained 250 ng.

[b] Identifications were based on criteria established in the wastewater screening protocol. Background levels were used for recovery determinations only and were not verified from full scan spectra.

[c] Recovery ± standard deviation for triplicate determinations.

[d] ND = not detected.

[e] Large interfering peaks observed in data for one of the unfortified samples were not observed in the fortified samples. Recoveries were calculated assuming no vinyl chloride in the unspiked sludge.

from wastewaters. Based on this recovery data, the modified purge-trap GC/MS method described above was included in a preliminary protocol for analyses of POTW sludges.[4]

ADDITIONAL METHODS DEVELOPMENT FOR MUNICIPAL AND INDUSTRIAL WASTEWATER TREATMENT SLUDGE

The primary weakness of the preliminary purge-trap GC/MS method developed for sludge was poor reproducibility. In addition, dilution to control foaming decreased the effective detection limits for the analytes. Although recoveries of spiked compounds are typical of those observed for highly polluted wastewaters, the precision of recovery determinations observed were ± 40 to 50% relative standard deviation. The experiments described below were designed to develop a purging procedure with improved recoveries, reproducibility, and detection limits. A comparison of recoveries from spiked sludge and sludge supernatant was conducted to investigate the relative influences of dissolved and suspended solids on volatiles purging. The feasibility of using salt or organic additives to improve purging reproducibility was investigated. Finally, alternate purging systems incorporating mechanical mixing were evaluated to enhance analyte transfer to the purge gas stream.

Recovery of Spikes from Sludge and Sludge Supernatant

Experimental--

Four 100-ml aliquots of primary POTW sludge (4.8% solids) were centrifuged at 3,000 rpm for 1 h in 250-ml centrifuge tubes. The supernatants were decanted into 40-ml screw-cap vials containing two stainless steel balls, and the vials were sealed with no headspace with TFE-lined septa. Additional vials were prepared with aliquots of the same sludge that had not been centrifuged. Triplicate vials of sludge and sludge supernatant were spiked with the purgeable test compounds at 250 μg/liter. All vials were allowed to equilibrate overnight at 4°C, with tumbling, prior to analysis. Duplicate unspiked and triplicate spiked aliquots were analyzed by the purge-trap GC/MS procedures described in the preliminary POTW sludge protocol.

Results and Discussion--

The results of the recovery determinations are shown in Table 3. The primary sludge selected for this experiment contained very high concentrations of vinyl chloride. Hence, recovery of the vinyl chloride spike was not observed. The recoveries for the spiked compounds from the sludge supernatant were both higher and less variable than from the unfractionated sludge for all compounds. Furthermore, the range of recoveries observed for the supernatant aliquots was similar to those typically observed for spiked clean water. Spike recoveries from the sludge supernatant aliquots in excess of 100% may reflect slightly lower recoveries for the internal quantitation standards relative to the analytes. Nonetheless, it is likely that the presence of dissolved solids in the primary sludge do not significantly affect the purging efficiencies of the spiked compounds. Subsequent experiments were focused on examining procedures with a potential for enhancing the release of analytes from the suspended solids.

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[4] Midwest Research Institute. Analytical Protocol for Screening Publicly Owned Treatment Works (POTW) Sludges for Organic Priority Pollutants. Special Report No. 1 to EPA under Contract No. 68-03-2695, June 1979.

TABLE 3. RECOVERIES OF PURGEABLE COMPOUNDS FROM UNSPIKED AND SPIKED PRIMARY SLUDGE AND PRIMARY SLUDGE SUPERNATANT BY PURGE-TRAP GC/MS

Compound	Nominal spike level (μg/L)	Sludge		Sludge supernatant	
		Unfortified concentration (μg/L)	Spike recovery (%)	Unfortified concentration (μg/L)	Spike recovery (%)
Benzene	250	ND[a]	58 ± 54[b]	ND	130 ± 11
Carbon	250	ND	47 ± 58	ND	110 ± 13
Chloroform	250	ND	37 ± 20	ND	120 ± 14
1,1-Dichloroethene	250	ND	52 ± 33	ND	120 ± 20
Tetrachloroethene	250	10	72 ± 53	ND	90 ± 14
Vinyl chloride[c]	250	~ 4,100	-	-	-
1,2-Dichloroethane	250	ND	71 ± 44	ND	120 ± 13
Trichloroethene	250	6	53 ± 42	ND	110 ± 16
1,1,1-Trichloroethane	250	59	83 ± 54	ND	120 ± 14
Chlorobenzene	250	ND	61 ± 44	ND	100 ± 5
Ethylbenzene	250	325	d	27	95 ± 12

[a] ND = not detected.

[b] Recovery ± standard deviation for triplicate determinations.

[c] Present in sludge at very high concentrations beyond the method dynamic range. Not quantitated in sludge fractions.

[d] Concentration in spiked sludge not determined because of peak saturation.

Evaluation of the Addition of Salt or a High Boiling Organic to Enhance Purging Efficiencies

The addition to sludge aliquots of salt or a high boiling, hydrophilic organic compound, which has very low tendency to purge from water, prior to purging was evaluated as a means of enhancing the purging efficiencies of volatile compounds, or at least improving the reproducibility of purging. The recoveries of compounds spiked into sludge and sludge supernatant indicated that interactions of the purgeable compounds with the suspended solids may have a significant influence on their purging efficiencies. The addition of salt or a high boiling organic was an attempt to favorably alter those interactions and to provide a consistent matrix for purging. Adding salt may enhance the purging efficiencies for some compounds by decreasing their solubilities in the aqueous sludge matrix. However, increasing the polarity of the matrix may encourage stronger association of some compounds with the sludge solids and decrease their availability for purging. Alternatively, the addition of a high boiling, hydrophilic organic may lower the polarity of the matrix and encourage desorption of analytes from solids while tending to retard purging efficiencies. In either case, modification of the sludge matrix to a relatively consistent polarity may improve the reproducibility of recoveries, whatever the effects on the magnitude of recoveries. Preliminary experiments were conducted to determine the responses of the purgeable spiking compounds spiked into clean water and purged following addition of salt or ethylene glycol. Ethylene glycol was selected as the organic additive because of its low volatility, good aqueous solubility, and general availability. The influence of salt and ethylene glycol additives on purging efficiencies from clean water and recoveries from primary POTW sludge were also evaluated.

Comparison of Relative Purging Efficiencies from Clean Water and Clean Water with Salt or Ethylene Glycol Added--

Experimental--Aliquots (2.0 ml) of volatiles-free water were spiked with 100 ng of each of the purgeable spiking compounds and three internal standards bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane, diluted to 10 ml with one of three dilution waters, and then analyzed by purge-trap gas chromatography with a flame ionization detector (GC/FID). Areas of well-resolved peaks were measured with the aid of a chromatographic integrator. The responses of compounds exhibiting poorly resolved or merged peaks were determined by manual measurement of peak heights. The three dilution waters utilized were: (a) volatiles-free water, (b) saturated sodium chloride in volatiles-free water, and (c) 10% ethylene glycol in volatiles-free water. To avoid bias caused by day-to-day variations in detector response, the compound responses for aliquots diluted with salt water or ethylene glycol-water were compared with responses for water-diluted aliquots on each day of analysis.

Results and discussion--The chromatographic responses observed for the purgeable compounds spiked into water and water with salt are shown in Table 4. Table 5 shows a similar comparison for compounds spiked into water and water with ethylene glycol. The purging of most compounds does not appear to be significantly perturbated by the addition of salt or ethylene glycol. Chloroform and 1,2-dichloroethane exhibited a slightly higher response in water when

TABLE 4. CHROMATOGRAPHIC RESPONSES FOR PURGEABLE COMPOUNDS SPIKED INTO WATER AND WATER WITH SALT

Compound	Peak area[a] or height					
	Water Blank		10-ng standard			
	No salt	With salt	No salt	No salt	With salt	With salt
1,1-Dichloroethene[b]	ND[c]	ND	14.5	11.0	9.0	9.5
Chloroform	16.5	20.4	345	316	525	517
1,2-Dichloroethane	ND	ND	48.6	49.1	74.3	61.3
1,1,1-Trichloroethane	ND	ND	28.4	35.2	30.8	33.2
Carbon tetrachloride	ND	ND	9.8	10.8	7.8	8.2
Trichloroethene & benzene[d]	2.7	1.9	283	284	269	267
Tetrachloroethene	ND	ND	40.8	41.3	47.5	41.5
Chlorobenzene	132	92.3	315	366	282	410
Ethylbenzene	ND	ND	260	386	252	359
Internal standards						
Bromochloromethane[b]	12.0	12.0	12.0	11.5	11.0	10.5
2-Bromo-1-chloropropane	68.1	61.4	68.1	67.1	54.9	54.4
1,4-Dichlorobutane	59.6	91.6	60.6	67.8	97.8	95.4

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[a] Dimensionless area units.

[b] Responses determined by peak height (mm).

[c] ND = not detected.

[d] These compounds coeluted and were indistinguishable by GC/FID.

TABLE 5. CHROMATOGRAPHIC RESPONSES FOR PURGEABLES SPIKED INTO WATER AND WATER WITH ETHYLENE GLYCOL

Compound	Peak area[a] or height							
	Water blank		100-ng standard					
	No $Et(OH)_2$	With $Et(OH)_2$	No $Et(OH)_2$	No $Et(OH)_2$	No $Et(OH)_2$	With $Et(OH)_2$	With $Et(OH)_2$	With $Et(OH)_2$
1,1-Dichloroethene[b]	ND[e]	ND	7.5	7.0	7.0	7.0	10.0	7.0
Chloroform	ND	ND	48.3	67.0	88.1	98.7	97.1	98.1
1,2-Dichloroethane	ND	ND	50.6	51.6	48.5	52.1	50.9	51.3
1,1,1-Trichloroethane	ND	ND	36.0	33.0	32.7	42.2	40.6	44.8
Carbon tetrachloride	ND	ND	10.0	8.9	9.7	13.9	13.0	8.7
Trichloroethene & benzene[d]	ND	ND	325	299	299	720	687	680
Tetrachloroethene	ND	ND	48.3	42.2	43.7	52.7	45.7	43.5
Chlorobenzene	ND	ND	371	282	298	416	424	280
Ethylbenzene	ND	ND	321	278	277	287	427	279
Internal standards								
Bromochloromethane[b]	10.0	10.0	10.0	8.0	9.0	10.0	9.0	9.0
2-Bromo-1-chloropropane	66.9	66.3	73.4	70.7	71.8	69.9	61.4	67.6
1,4-Dichlorobutane	55.8	73.9	66.1	58.9	57.0	64.4	57.4	59.5

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a Dimensionless area units.

b Responses determined by peak height (mm).

c ND = not detected.

d These compounds coeluted and were indistinguishable by GC/FID.

salt was added. However, the responses for chloroform and 1,1,1-trichloroethane were slightly higher in water plus ethylene glycol. The coeluting compounds, trichloroethene and benzene, produced a response more than two times higher in the ethylene glycol spiked solution. The addition of salt or ethylene glycol did not appear to decrease the response of any compound.

Evaluation of Spike Recoveries for Primary Sludge Aliquots Diluted with Saturated Salt or 10% Ethylene Glycol in Water--

Experimental--Primary sludge (2% solid content) was poured into five 40-ml screw-cap vials containing five stainless steel balls each. The vials were sealed with no headspace with TFE-lined septa. Triplicate vials were spiked with the purgeable spiking compounds at 100 ng/ml. Standards were prepared at the same time by spiking volatiles-free water. All vials were allowed to equilibrate at 4°C overnight, with tumbling, prior to analysis. Aliquots (2.5 ml) of the duplicate unspiked and triplicate spiked samples were diluted to 10 ml with either saturated salt solution or 10% ethylene glycol and then analyzed by GC/MS using the preliminary POTW protocol procedures.

Results and discussion--The recoveries of spiked purgeable compounds in sludge analyzed following dilution with salt and ethylene glycol solutions are shown in Tables 6 and 7, respectively.

No specific advantages from adding salt or ethylene glycol were apparent. Recoveries for all compounds were generally good. Recoveries for some compounds in excess of 100% may indicate slightly lowered purging efficiencies for the internal standards. Recoveries for carbon tetrachloride were significantly higher than typically observed using the preliminary POTW sludge protocol. However, both additives appeared to significantly increase the tendency of the sludge to foam during purging. Hence, the use of salt and ethylene glycol in sludge dilutions did not provide significant overall improvements from the preliminary POTW sludge protocol.

Evaluation of Alternate Purging Systems

Alternate purging hardware systems which provide mechanical mixing during purging were evaluated for the analysis of purgeables in sludge. Mechanical agitation of the sludge may enhance desorption of analytes from the sludge solids to the supernatant and improve transfer to the purge gas stream. All systems evaluated were designed to be used as direct replacements for the conventional purge tube in the purge-trap system employed in the preliminary POTW sludge protocol. Four hardware systems were evaluated. Three configurations were fabricated using a small round-bottom flask: stirred purging, stirred impinging, and sonicated impinging. The fourth system evaluated was a stirred purge configuration using a specially designed bottom frit tube.

Purging Systems Configured with a Round-Bottom Flask--

The efficiencies of transfer of volatile compounds from aqueous solution to the gas phase afforded by the stirred purging, stirred impinger, and sonicated impinger systems were evaluated by comparing the chromatographic responses for compounds spiked into water and analyzed with these systems. The chromatographic responses for identical solutions were analyzed via the conventional purge tube.

TABLE 6. RECOVERIES OF PURGEABLE COMPOUNDS BY PURGE-TRAP GC/MS FROM SPIKED PRIMARY SLUDGE DILUTED WITH A SATURATED SALT SOLUTION

Compound	Spike level (ng)	Unspiked sludge (ng)[a]	Spike recovery[b] (%)
Benzene	250	10.8, 30.6	170 ± 48
Carbon tetrachloride	250	ND, ND[c]	59 ± 22
Chloroform	250	16.9, 12.0	172 ± 32
1,1-Dichloroethene	250	15.4, 20.5	219 ± 54
Tetrachloroethene[d]	250	-	-
1,2-Dichloroethane	250	4.5, 4.8	123 ± 22
Trichloroethene	250	322, 364	e
1,1,1-Trichloroethane	250	ND, ND	115 ± 37
Chlorobenzene	250	6.6, 5.7	125 ± 15
Ethylbenzene	250	33.6, 75.0	97 ± 12

a 2.5-ml sludge aliquot.

b Mean recovery ± standard deviation for triplicate determinations.

c ND = not detected.

d Ion plots for all unspiked and spiked samples exhibited saturated peaks.

e Ion plots for spiked sludge samples exhibited saturated peaks.

TABLE 7. RECOVERIES OF PURGEABLE COMPOUNDS BY PURGE-TRAP GC/MS FROM SPIKED PRIMARY SLUDGE DILUTED WITH A 10% ETHYLENE GLYCOL SOLUTION

Compound	Spike level (ng)	Unspiked sludge (ng)[a]	Spike recovery[b] (%)
Benzene	250	ND, ND[c]	108 ± 24
Carbon tetrachloride	250	ND, ND	81 ± 12
Chloroform	250	8.7, 9.8	130 ± 30
1,1-Dichloroethene	250	19.7, 10.0	134 ± 34
Tetrachloroethene[d]	250	-	-
1,2-Dichloroethane	250	ND, ND	100 ± 30
Trichloroethene	250	215, 190	-[e]
1,1,1-Trichloroethane	250	ND, ND	130 ± 42
Chlorobenzene	250	7.7, 6.3	119 ± 6
Ethylbenzene	250	36.5, 52.4	95 ± 12

a 2.5-ml sludge aliquot.

b Mean recovery ± standard deviation for triplicate determinations.

c ND = not detected.

d Ion plots for all unspiked and spiked samples exhibited saturated peaks.

e Ion plots for spiked sludge samples exhibited saturated peaks.

Experimental--The stirred purge and stirred impinger systems were assembled as shown in Figures 5 and 6, respectively. A 100-ml round-bottom flask was fitted with a magnetic stir bar. The purging gas entered the flask via a fritted tube placed under the surface of the diluted sample. The same flask was utilized for the stirred and sonicated dynamic headspace systems except that the fritted tube was placed above the surface of the diluted sample. Sonication was accomplished by removing the magnetic stirring system and placing the flask in a small sonic cleaner bath filled with 2 to 3 cm of water. All three systems were evaluated by comparing the GC/FID or GC/MS responses with those from the conventional purge tube for the purgeable spiking compounds and the purgeable internal standards spiked into clean water at 100 ng. The stirred purge and stirred dynamic headspace systems were charged with 50 ml of water. The sonicated dynamic headspace system was charged with 10 ml so that levels of the water in the bath and the flask were approximately equal.

Results and discussion--The chromatographic responses obtained for two consecutive days of comparisons of stirred purge, stirred dynamic headspace, and conventional purge extraction of the purgeables spiking compounds using GC/MS analysis are shown in Tables 8 and 9. In general, the responses obtained from using stirred purge and dynamic headspace were lower than those from the conventional purge tube. In particular, the internal standard responses were markedly lower. Table 10 shows the chromatographic responses comparing sonicated dynamic headspace with conventional purging with GC/FID. Again the responses from the conventional purging system were higher for most compounds. From these results, it appears that the geometry of the conventional purge tube, i.e., a small diameter column with gas bubbling from a frit at the bottom to the surface of the sample, provides better transfer of purgeable organics from the sample to the gas stream, at least for clean water samples.

Purging System Configured with an MRI-Designed Stirred Bottom Frit Tube--

In order to combine the advantages of the conventional purge tube geometry with mechanical agitation, a purge tube was designed and fabricated to allow the use of a magnetic stirrer. The diameter of the tube was increased to provide more cross-sectional area of sample headspace to reduce the potential for foaming. The modified purge tube, referred to hereafter as a "bottom frit tube," is shown in Figure 7. The performance of the bottom frit tube with and without mechanical stirring was compared with that of the conventional purge tube for spiked water. The MRI-designed tube was similarly evaluated with spiked sludge with stirring and with sonication.

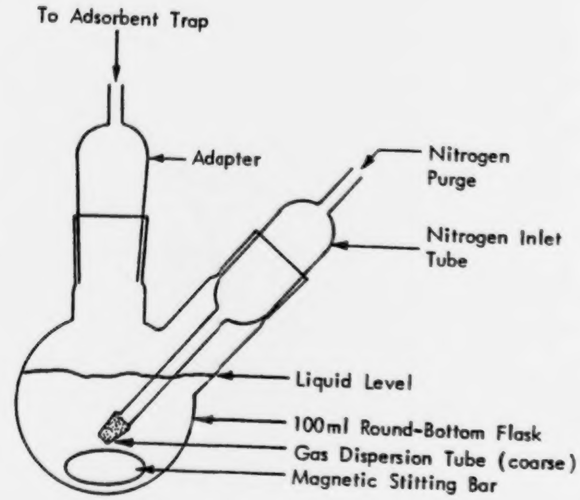
To Adsorbent Trap
Adapter
Nitrogen Purge
Nitrogen Inlet Tube
Liquid Level
100ml Round-Bottom Flask
Gas Dispersion Tube (coarse)
Magnetic Stitting Bar

Figure 5. Stirred purging system using a round-bottom flask.

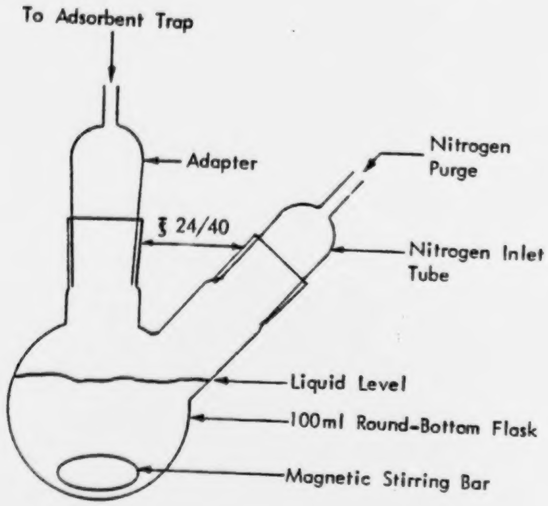
To Adsorbent Trap
Adapter
₹ 24/40
Nitrogen Purge
Nitrogen Inlet Tube
Liquid Level
100ml Round-Bottom Flask
Magnetic Stirring Bar

Figure 6. Stirred impinger system using a round-bottom flask.

TABLE 8. CHROMATOGRAPHIC RESPONSES FOR PURGEABLES SPIKED INTO CLEAN WATER AND ANALYZED BY PURGE-, STIRRED PURGE-, AND STIRRED DYNAMIC HEADSPACE-TRAP GC/MS - DAY 1

	Peak height (mm)					
	Water blank			100-ng standard		
Compound	Purge tube	Stirred purge	Dynamic headspace	Purge tube	Stirred purge	Dynamic headspace
1,1-Dichloroethene	ND[a]	ND	ND	6.0	5.5, 5.0	6.0
Chloroform	ND	ND	ND	20.0	13.5, 13.5	8.5
1,2-Dichloroethane	ND	ND	ND	13.0	5.0, 3.5	7.5
1,1,1-Trichloroethane	ND	ND	ND	1.5	2.0, 2.0	1.5
Carbon tetrachloride	ND	ND	ND	2.0	2.0, ND	0.5
Trichloroethene	ND	ND	ND	20.0	21.0, 17.0	17.5
Benzene	2.0	5.0	2.0	77.0	67.0, 71.0	68.0
Tetrachloroethene	ND	ND	ND	20.0	16.5, 19.0	15.0
Chlorobenzene	ND	ND	ND	63.5	52.0, 42.5	41.0
Ethylbenzene	5.0	7.5	1.5	24.5	25.0, 21.0	24.0
Internal standards						
Bromochloromethane	31.0	14.0	8.5	30.0	12.0, 11.5	11.0
2-Bromo-1-chloropropane	34.0	20.0	14.5	41.0	17.0, 19.0	17.0
1,4-Dichlorobutane	52.5	13.0	10.0	54.5	15.0, 16.0	20.5

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[a] ND = not detected.

TABLE 9. CHROMATOGRAPHIC RESPONSES FOR PURGEABLES SPIKED INTO CLEAN WATER AND ANALYZED BY PURGE-, STIRRED PURGE-, AND STIRRED DYNAMIC HEADSPACE-TRAP GC/MS - DAY 2

Compound	Peak height (mm)					
	Water blank			100-ng standard		
	Purge tube	Stirred purge	Stirred[a] dynamic headspace	Purge tube	Stirred purge	Stirred dynamic headspace
1,1-Dichloroethene	ND[b]	ND		4.5, 4.5	5.0	5.0, 4.5
Chloroform	ND	ND		15.5, 13.0	12.0	10.5, 10.5
1,2-Dichloroethane	ND	ND		11.5, 12.0	3.5	4.0, 5.0
1,1,1-Trichloroethane	ND	ND		1.5, 1.5	1.5	2.0, 1.5
Carbon tetrachloride	ND	ND		2.0, 2.0	0.5	ND, 0.5
Trichloroethene	ND	ND		17.5, 18.5	19.5	14.0, 14.5
Benzene	2.0	2.5		65.6, 71.0	63.0	51.0, 53.0
Tetrachloroethene	ND	ND		12.0, 14.0	17.0	14.0, 11.5
Chlorobenzene	ND	ND		54.0, 57.0	44.0	41.0, 36
Ethylbenzene	1.5	4.0		22.0, 18.5	20.0	19.0, 18.0
Internal standards						
Bromochloromethane	25.0	9.0		26.0, 25.0	14.0	12.0, 8.0
2-Bromo-1-chloropropane	35.0	12.0		29.0, 29.0	16.0	15.0, 10.0
1,4-Dichlorobutane	43.5	12.0		46.0, 50.0	15.0	16.0, 18.0

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[a] Not analyzed.

[b] ND = not detected.

TABLE 10. CHROMATOGRAPHIC RESPONSES FOR PURGEABLES SPIKED INTO CLEAN WATER AND ANALYZED BY PURGE- AND SONICATED DYNAMIC HEADSPACE-TRAP GC/FID

	Peak area[a] or height (mm)			
	Water blank		100-ng standard	
Compound	Purge tube	Sonicated dynamic headspace	Purge tube	Sonicated dynamic headspace
1,1-Dichloroethene	ND[b]	ND	13	4.0 ± 0[c]
Chloroform	5.4	4.4	52.3, 51.7	32.3 ± 5.2
1,2-Dichloroethane	ND	ND	58.4, 56.1	28.4 ± 3.6
1,1,1-Trichloroethane	ND	ND	35.8, 32.4	24.6 ± 3.6
Carbon tetrachloride	ND	0.2	13.7, 12.8	12.0 ± 2.4
Trichloroethene & benzene[d]	3.6	11.5	387, 403	196 ± 51
Tetrachloroethene	21.2	ND	54.4, 58.2	43.1 ± 3.5
Chlorobenzene	ND	7.0	414, 420	189 ± 58
Ethylbenzene	76.1	6.9	474, 444	284 ± 86
Internal standards				
Bromochloromethane	19.8	15.0	13, 11	17.0 ± 2.9
2-Bromo-1-chloropropane	77.9	41.3	80.2, 68.9	49.6 ± 8.3
1,4-Dichlorobutane	99.8	47.5	88.5	52.6 ± 10.4

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[a] Area units measured with an LDC Model 308 integrator.

[b] ND = not detected.

[c] Mean response ± standard deviation for three determinations.

[d] These compounds coeluted and were indistinguishable by GC/FID.

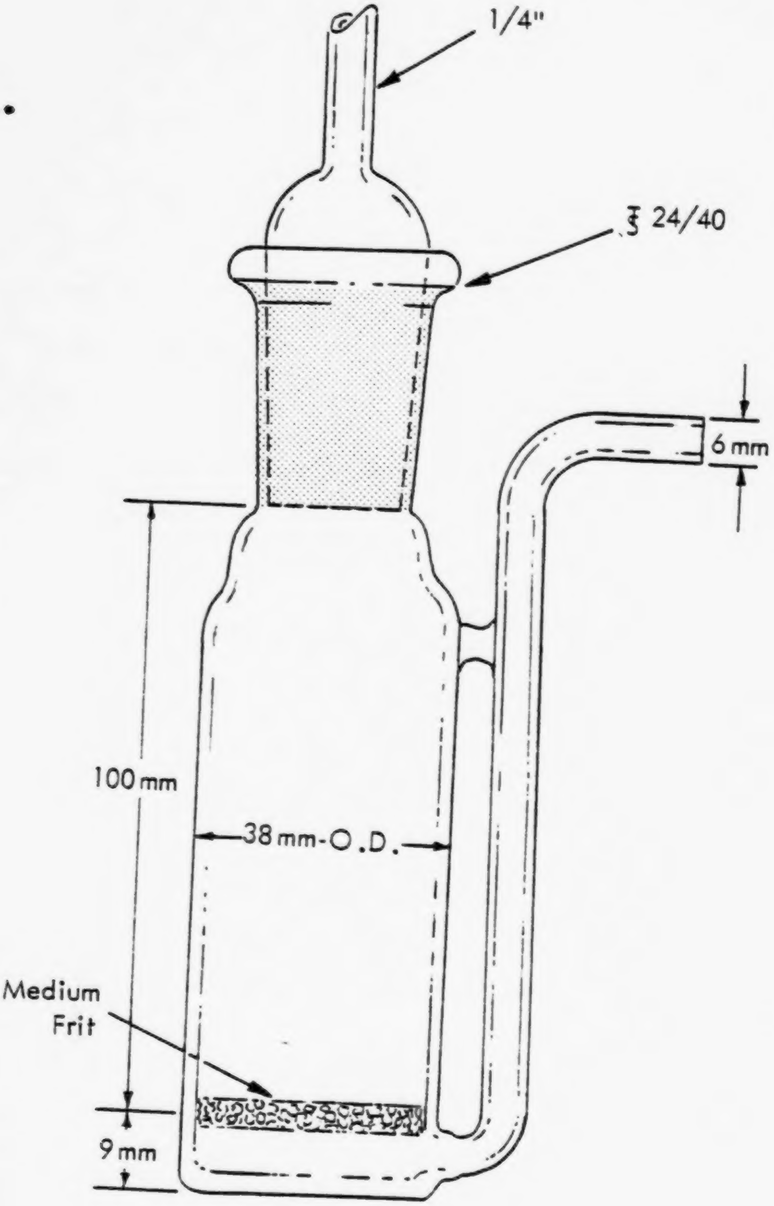
1/4"
Ṩ 24/40
6 mm
100 mm
38 mm-O.D.
Medium Frit
9 mm

Figure 7. Bottom frit purge tube.

Preliminary evaluations--

Experimental--Aliquots of volatiles-free water (10.0 ml) were spiked with 100 ng of each of the purgeable spiking compounds and the three internal standard compounds, bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane. The spiked samples were then analyzed by purge-trap GC/FID using conventional purge tube and the bottom frit tube with and without stirring. Areas of well-resolved peaks were measured with the aid of a chromatographic integrator. The responses of compounds exhibiting poorly resolved or merged peaks were determined by manual measurement of peak heights. The chromatographic responses of compounds analyzed with the bottom frit purge apparatus with and without stirring were compared with the responses obtained using conventional purge tube.

Sludge aliquots (2.5 ml) were spiked with 250 ng of each of the purgeable spiking compounds, immediately diluted to 10 ml with volatiles-free water, and analyzed by GC/MS using the preliminary POTW protocol procedures. The recoveries were determined for the purgeable spiking compounds from spiked sludge using the bottom frit tube apparatus with sonication and stirring.

Results and discussion--The chromatographic responses for the purgeable compounds spiked into water by conventional purge tube and bottom frit tube without stirring are shown in Table 11. Table 12 shows a similar comparison for purge tube and the stirred bottom frit tube. The responses observed for a few compounds analyzed in spiked water with the bottom frit tube without stirring were lower than those from the conventional purge tube. The bottom frit tube with stirring produced responses generally as high or higher than the conventional tube. These results likely reflect poorer contact of the sparging bubbles with the water in the unstirred bottom frit tube relative to the conventional purge tube. The purge flow (40 ml/min) produces only one or two streams of bubbles across the frit of the bottom frit tube. Since the 10-ml aliquot occupies a shorter portion of tube in the wider bottom frit apparatus, the residence time of a single bubble in the aliquot is less than in the conventional purge tube. Stirring the bottom frit tube causes the bubbles to swirl through the sample and increases the residence time of bubbles in the aliquot. Hence, stirring is necessary to obtain satisfactory purging using the bottom frit tube.

Recoveries of the purgeable compounds from spiked sludge by the bottom frit tube with stirred purging and with sonicated purging are shown in Tables 13 and 14, respectively. Good recovery data were obtained using the modified bottom frit tube for all the compounds except carbon tetrachloride. This was most likely due to the low sensitivity of carbon tetrachloride to GC/MS.*

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* Low sensitivity has been frequently observed for carbon tetrachloride. This likely results from a combination of the poor chromatographic peak shape characteristic of this compound and its characteristic fragmentation. The principal ions are frequently obscured by coeluting background materials.

TABLE 11. CHROMATOGRAPHIC RESPONSES FOR PURGEABLES SPIKED INTO CLEAN WATER AND ANALYZED BY PURGE TUBE AND BOTTOM FRIT TUBE WITHOUT STIRRING

Compound	Peak area[a] or height (mm)			
	Water blank		100-ng standard	
	Purge tube	Bottom frit tube	Purge tube	Bottom frit tube
1,1-Dichloroethene[b]	ND[c]	ND	200, 200	196 ± 7[d]
Chloroform	ND	ND	21.4, 23.0	18 ± 1
1,2-Dichloroethane	ND	ND	50.1, 53.2	42 ± 2
1,1,1-Trichloroethane	ND	ND	61.2, 61.5	59 ± 2
Carbon tetrachloride	ND	ND	22.9, 24.1	21 ± 4
Trichloroethene & benzene[e]	ND	2.0	394, 404	323 ± 25
Tetrachloroethene[f]	-	-	-	-
Chlorobenzene	28, 19	8.3, 11	287, 269	187 ± 9
Ethylbenzene	0.9, 3.5	13, 5.3	339, 347	295 ± 14
Internal standards				
Bromochloromethane[b]	61, 58	29, 45	35.0, 35.0	37 ± 3
2-Bromo-1-chloropropane[g]	-	106, 104	-	114 ± 9
1,4-Dichlorobutane	70, 63	42, 64	135, 139	122 ± 6

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[a] Dimensionless area unit.

[b] Response determined by peak height (mm).

[c] ND = not detected.

[d] Mean ± standard deviation for triplicate determinations.

[e] These compounds coeluted and were indistinguishable by GC/FID.

[f] Interferences in the blank water did not allow measurement of this compound.

[g] Severe interferences prevented measurement of this compound from the conventional purge tube.

TABLE 12. CHROMATOGRAPHIC RESPONSES FOR PURGEABLES SPIKED INTO CLEAN WATER AND ANALYZED BY PURGE TUBE AND STIRRED BOTTOM FRIT TUBE

	Peak area[a] or height (mm)			
	Water blank		100-ng standard	
Compound	Purge tube	Stirred bottom frit tube	Purge tube	Stirred bottom frit tube
1,1-Dichloroethene[b]	ND[c]	ND	30	45, 35
Chloroform	79	61.1 ± 14.8[d]	851	791
1,2-Dichloroethane	1.6	ND	43	44
1,1,1-Trichloroethane	0.8	3.5 ± 1.5	24	22, 27
Carbon tetrachloride	0.8	2.5 ± 2.4	9.2	7.7, 10.6
Trichloroethene & benzene[e]	7.4	6.2 ± 6.1	236	260, 242
Tetrachloroethene	ND	ND	35	46
Chlorobenzene	22	7.2 ± 2.7	175	252, 246
Ethylbenzene	3.5	1.9 ± 2.7	233	416, 310
Internal standards				
Bromochloromethane[b]	52	38.7 ± 1.2	35	45, 40
2-Bromo-1-chloropropane	69	61.6 ± 3.6	59	77, 63
1,4-Dichlorobutane	74	66.2 ± 13.2	64	73

[a] Dimensionless area unit.

[b] Response determined by peak height (mm).

[c] ND = not detected.

[d] Mean ± standard deviation for triplicate determinations.

[e] These compounds coeluted and were indistinguishable by GC/FID.

TABLE 13. RECOVERIES OF PURGEABLE COMPOUNDS FROM SPIKED SLUDGE BY STIRRED PURGING WITH A BOTTOM FRIT TUBE

Compound	Spike level (ng)	Unspiked sludge (ng)[a]	Spike recovery[b] (%)
Benzene	250	ND, ND[c]	113 ± 10
Carbon tetrachloride	250	ND, ND	0 ± 0
Chloroform	250	8.6, 2.3	117 ± 8
1,1-Dichloroethene	250	7.5, 6.0	123 ± 6
Tetrachloroethene[d]	250	-	-
1,2-Dichloroethane	250	ND, ND	108 ± 4
Trichloroethene	250	217, 347	-[e]
1,1,1-Trichloroethane	250	ND, ND	106 ± 17
Chlorobenzene[f]	250	19, 13	145 ± 4
Ethylbenzene	250	51, 45	101 ± 11

[a] 2.5-ml sludge aliquot.

[b] Mean recovery ± standard deviation for triplicate determinations.

[c] ND = not detected.

[d] Ion plots for all unspiked and spiked samples exhibited saturated peaks.

[e] Ion plots for spiked sludge samples exhibited saturated peaks.

[f] Peak interferences.

TABLE 14. RECOVERIES OF PURGEABLE COMPOUNDS FROM SPIKED SLUDGE BY SONICATED PURGING WITH A BOTTOM FRIT TUBE

Compound	Spike level (ng)	Unspiked sludge (ng)[a]	Spike recovery[b] (%)
Benzene	250	18, 23	132 ± 30
Carbon tetrachloride	250	ND, ND[c]	0 ± 0
Chloroform	250	14, 11	115 ± 26
1,1-Dichloroethene	250	16, 26	137 ± 42
Tetrachloroethene[d]	250	-	-
1,2-Dichloroethane	250	15, 16	106 ± 14
Trichloroethene	250	201, 234	-[e]
1,1,1-Trichloroethane	250	ND, ND	88 ± 19
Chlorobenzene	250	10, 9	95 ± 18
Ethylbenzene	250	42, 44	115 ± 31

[a] 2.5-ml sludge aliquot.

[b] Mean recovery ± standard deviation for triplicate determinations.

[c] ND = not detected.

[d] Ion plots for all unspiked and spiked samples exhibited saturated peaks.

[e] Ion plots for spiked sludge samples exhibit saturated peaks.

The carbon tetrachloride response was too low to determine under the specific GC/MS operating conditions utilized. Recoveries were more reproducible for most compounds with the stirred system. These data and the observation that the stirred system appeared to produce much better agitation than sonication indicated that the stirred bottom frit tube may provide significant advantages over the conventional purge tube. An additional advantage was that no foaming was observed with the bottom frit tube whereas aliquots of the same sample purged in the conventional purge tube foamed profusely.

Evaluation of purging large aliquots of sludge--Since good accuracy and precision data were obtained with the stirred bottom frit tube and there was no appreciable foaming, the system was evaluated for its capability to purge larger aliquots of sludge without troublesome foaming.

Experimental--Aliquots of 2.5, 5.0, and 10.0 ml of primary sludge (2% solids) were spiked with 250 ng of each of the purgeable spiking compounds just prior to analysis, diluted as required to 10 ml with volatiles-free water, and analyzed by the preliminary POTW sludge GC/MS procedures.

Results and discussion--The recoveries of the spiked purgeable compounds in different volumes of sludge are shown in Table 15. Recoveries for all compounds were good and did not appear to be strongly dependent on the volume of sludge purged. No foaming problems were encountered even with undiluted 10-ml aliquots. Evidently, the centrifugal force imparted by the magnetic stirring bar swirling sludge aliquot was an efficient foam dispersion mechanism.

Recoveries for spiked equilibrated sludge using the stirred bottom frit purge tube--In order to further evaluate the purging efficiencies afforded by the bottom frit tube and the practicality of purging larger aliquots of sludge, recoveries were determined for sludge samples allowed to equilibrate following spiking. In addition, the recoveries of purgeable compounds from spiked sludge using the stirred bottom frit tube were directly compared with those obtained using the conventional purge tube (specified in the preliminary POTW protocol).

Experimental--Primary sludge (2% solids) was poured into 40-ml screw-cap vials containing five stainless steel balls each. Three sets of duplicate vials were spiked with the purgeable spiking compounds at 100, 50, and 25 ng/ml, respectively, so that aliquots of 2.5, 5.0, and 10.0 ml sludge all contained 250 ng of spiking compounds. Standards were prepared at the same time by spiking volatiles-free water. All vials were allowed to equilibrate at 4°C overnight, with tumbling, prior to analysis. Aliquots of the spiked and unspiked sludge (2.5, 5.0, and 10.0 ml) were diluted as required to 10 ml with volatiles-free water and analyzed by the preliminary POTW sludge GC/MS procedures.

A similar experiment was conducted to directly compare recoveries from the conventional purge tube and the stirred bottom frit tube. A different primary sludge sample (3% solids) was used. The sludge was poured into 40-ml vials. The aliquots were spiked and allowed to equilibrate as described above. The conventional purge tube was used to analyze 2.0 ml aliquots; 2.0, 5.0, and 10.0-ml aliquots were analyzed with the bottom frit tube.

TABLE 15. RECOVERIES OF SPIKED PURGEABLE COMPOUNDS FROM SPIKED SLUDGE BY STIRRED PURGING WITH A BOTTOM FRIT TUBE: EFFECT OF DIFFERENT VOLUMES OF SLUDGE

Compound	Spike level (ng)	10-ml Aliquot unspiked sludge (ng)	Spike recovery (%)		
			2.5 ml	5 ml	10 ml
Benzene	250	49.2	133	142	148
Carbon tetrachloride	250	ND[a]	77	68	55
Chloroform	250	43.6	101	123	122
1,1-Dichloroethene	250	123	112	165	194
Tetrachloroethene[b]	250	-	-	-	-
1,2-Dichloroethane	250	ND	102	114	152
Trichloroethene[b]	250	-	-	-	-
1,1,1-Trichloroethane	250	ND	102	117	133
Chlorobenzene	250	19.0	135	108	61
Ethylbenzene[c]	250	118	-	-	-

[a] ND = not detected.

[b] Ion plots for all unspiked and spiked sample exhibited saturated peaks.

[c] Ion plots for all spiked sludge samples exhibited saturated peaks.

Results and discussion--The recoveries of the spiked purgeable compounds from 2.5, 5.0, and 10.0-ml sludge aliquots obtained by stirred purging with bottom frit tube are shown in Table 16. The recoveries were generally good. The recoveries did not appear to be dependent on the size of the aliquot purged even though the spike concentrations ranged from 100 µg/liter in the 2.5 ml aliquots to 25 µg/liter in the 10.0 ml aliquots. A comparison of recoveries of spikes obtained with the stirred bottom frit tube and with the conventional purge tube using a different primary POTW sludge is shown in Table 17. Recoveries of compounds in 10.0-ml aliquots of sludge spiked at 25 µg/liter analyzed with the stirred bottom frit tube were very similar to those in 2.0-ml aliquots of sludge spiked at 125 µg/liter using the conventional purge tube. In addition, no foaming was observed during stirred purging, even while purging 10.0-ml aliquots of undiluted sludge. Diluted aliquots of this sludge purged in the conventional tube foamed profusely. Two glass wool plugs were required in the top of the tube to control the foaming.

GC/MS chromatograms of unspiked and spiked sludge aliquots obtained with the stirred bottom frit tube and conventional purge tube are shown in Figures 8 through 15. Interestingly, the levels of background material in the sludge chromatograms were fairly consistent. Background levels were not significantly higher in chromatograms of the larger sludge aliquots analyzed with the stirred bottom frit tube. However, the level of late-eluting, unresolved material did appear to increase during any single analysis day, regardless of the purging system or sample aliquot size. Presumably, this was due to accumulation of materials on the GC column or the trap. The sludge background frequently obscured measurement of the response of two of the three internal standard compounds, especially bromochloromethane. Late-eluting materials also obscured measurement of responses from 1,4-dichlorobutane in some sludges. Only the second internal standard, 2-bromo-1-chloropropane, was consistently free of interferences. Although the composition of sludges varies widely, the frequency of interferences with bromochloromethane and with 1,4-dichlorobutane indicates that the selection of alternate early- and late-eluting internal standards may be required for some samples.

SELECTION OF METHODS FOR PURGEABLES IN SLUDGE

The simple adaptation of the industrial wastewater screening method[1] for sludges (dilution to approximately 0.5% solids prior to purging) developed for the preliminary POTW sludge protocol was not consistently successful in overcoming foaming problems during purging. Although recoveries observed for most compounds were good, recovery determinations were not very reproducible. In addition, sample dilution decreased the method detection limit. The stirred purge-trap GC/MS procedure using the MRI-designed bottom frit tube was demonstrated to provide significantly better reproducibility and better recoveries than were provided by the preliminary POTW protocol method. In addition, the capability of the stirred bottom frit procedure to purge 10.0-ml aliquots of undiluted sludge without appreciable foaming provides a significant improvement in method detection limits. Hence, the stirred bottom frit purge system was selected for a revised protocol for the analysis of purgeables in municipal and industrial wastewater treatment sludges. A detailed analytical protocol using this stirred purge-trap GC/MS method is appended to this report.

TABLE 16. RECOVERIES OF PURGEABLE COMPOUNDS FROM EQUILIBRATED SPIKED SLUDGE BY STIRRED PURGING WITH A BOTTOM FRIT TUBE: EFFECT OF DIFFERENT VOLUMES OF SLUDGE

Compound	Spike level (ng)	2.5-ml Aliquot sludge		5-ml Aliquot sludge		10-ml Aliquot sludge	
		Unspiked (ng)	Spike recovery (%)	Unspiked (ng)	Spike recovery (%)	Unspiked (ng)	Spike recovery (%)
Benzene	250	14	88, 118	22	122	93	148, 132
Carbon tetrachloride	250	ND[a]	22, 30	ND	32	ND	51, 50
Chloroform	250	11	66, 111	17	96	82	161, 158
1,1-Dichloroethene	250	15	127, 167	46	136	228	294, 258
Tetrachloroethene	250	1,378	b	1,962	b	5,029	b
1,2-Dichloroethane	250	ND	100, 135	ND	126	ND	133, 159
Trichloroethylene	250	427	27, 70	711	82	2,684	b
1,1,1-Trichloroethane	250	438	18, 56	733	70	2,578	b
Chlorobenzene	250	32	66, 73	56	83	134	75, 46
Ethylbenzene	250	78	59, 78	124	92	267	99, 63

a ND = Not detected.

b Recovery not determined since the level in the unspiked sample is much higher than the spike.

TABLE 17. RECOVERIES OF PURGEABLE COMPOUNDS FROM SPIKED SLUDGE BY STIRRED BOTTOM FRIT TUBE AND CONVENTIONAL PURGE TUBE

Compound	Spike level (ng)	2-ml Aliquot sludge		Stirred bottom frit tube				Conventional purge tube	
				5-ml Aliquot sludge		10-ml Aliquot sludge		2-ml Aliquot sludge	
		Unspiked (ng)	Spike recovery (%)	Unspiked (ng)	Spike recovery (%)	Unspiked (ng)	Spike recovery (%)	Unspiked (ng)	Spike recovery (%)
Benzene	250	9	118 ± 4[a]	16	90 ± 4	56	121, 121[b]	9	119, 112
Carbon tetrachloride	250	ND[c]	84 ± 4	ND	43 ± 6	ND	87, 90	ND	64, 61
Chloroform	250	ND	112 ± 15	ND	124 ± 10	ND	116, 126	ND	112, 104
1,1-Dichloroethene	250	1	113 ± 10	ND	98 ± 8	ND	150, 146	1	128, 100
Tetrachloroethene	250	9	145 ± 14	13	105 ± 6	22	88, 83	8	149, 117
Vinyl chloride	250	ND	125 ± 18	ND	112 ± 7	ND	122, 120	ND	123, 96
1,2-Dichloroethane	250	ND	109 ± 16	ND	121 ± 5	ND	121, 122	ND	124, 113
Trichloroethylene	250	38	115 ± 14	74	94 ± 7	204	122, 123	36	121, 114
1,1,1-Trichloroethane	250	ND	120 ± 20	ND	113 ± 6	ND	129, 128	2	126, 117
Chlorobenzene	250	ND	132 ± 5	5	92 ± 4	5	88, 69	8	138, 108
Ethylbenzene	250	40	138 ± 5	44	94 ± 4	99	80, 63	20	139, 104

a Mean recovery ± standard deviation for triplicate determination.

b Duplicate determinations.

c ND = not detected.

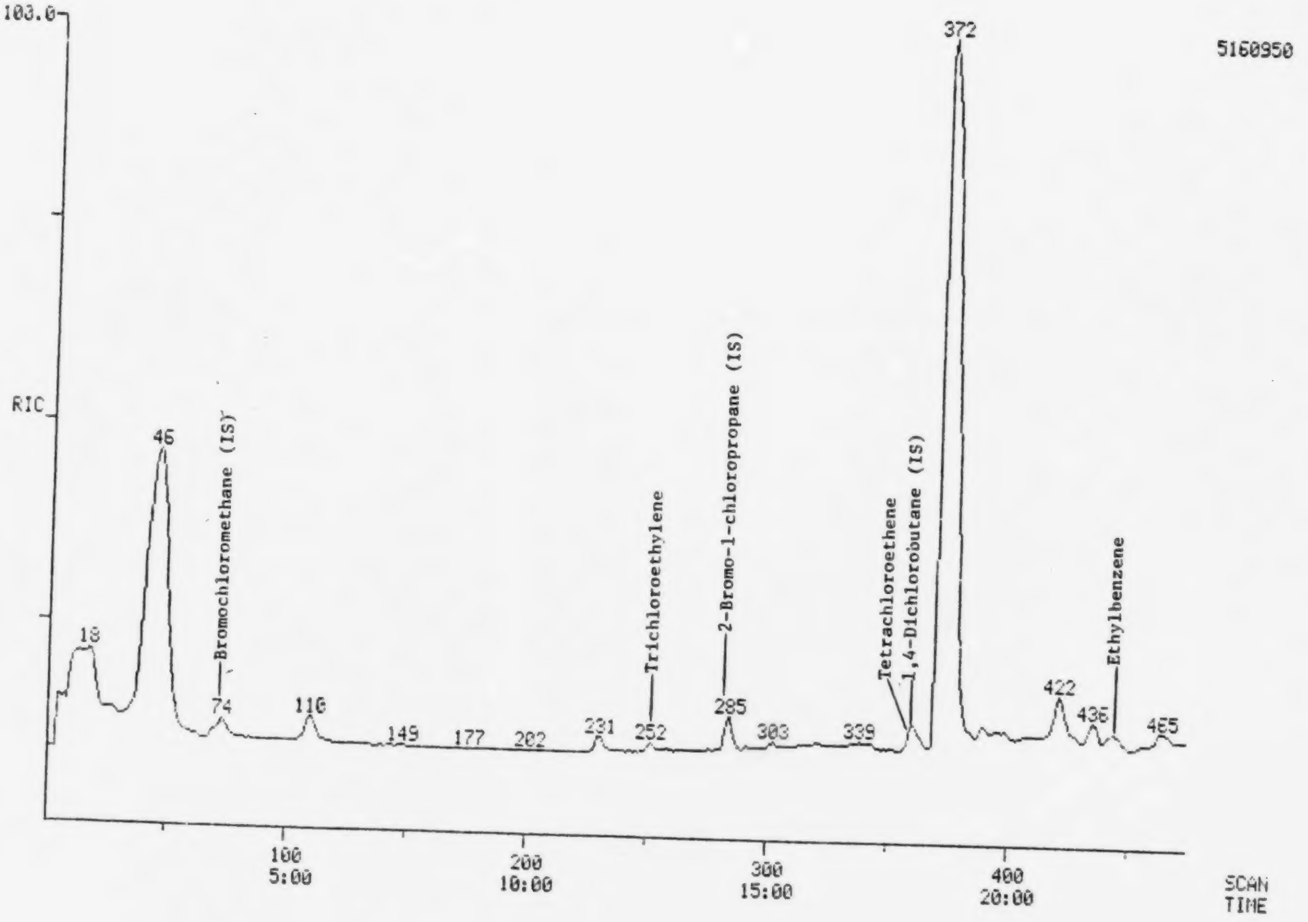

Figure 8. GC/MS chromatogram of a 2-ml aliquot of unspiked primary sludge analyzed with a stirred bottom frit tube.

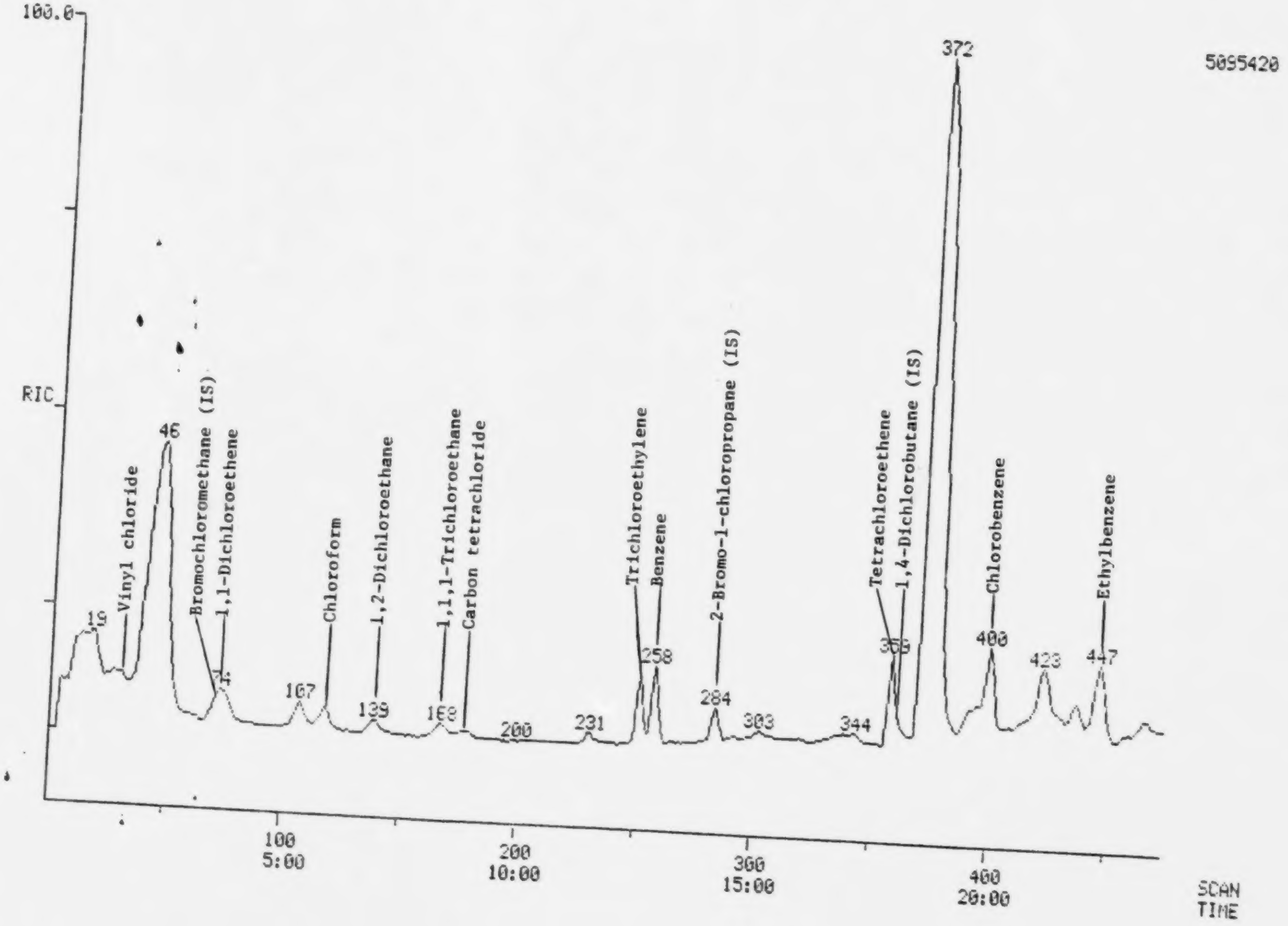

Figure 9. GC/MS chromatogram of a 2-ml aliquot of spiked primary sludge analyzed with a stirred bottom frit tube.

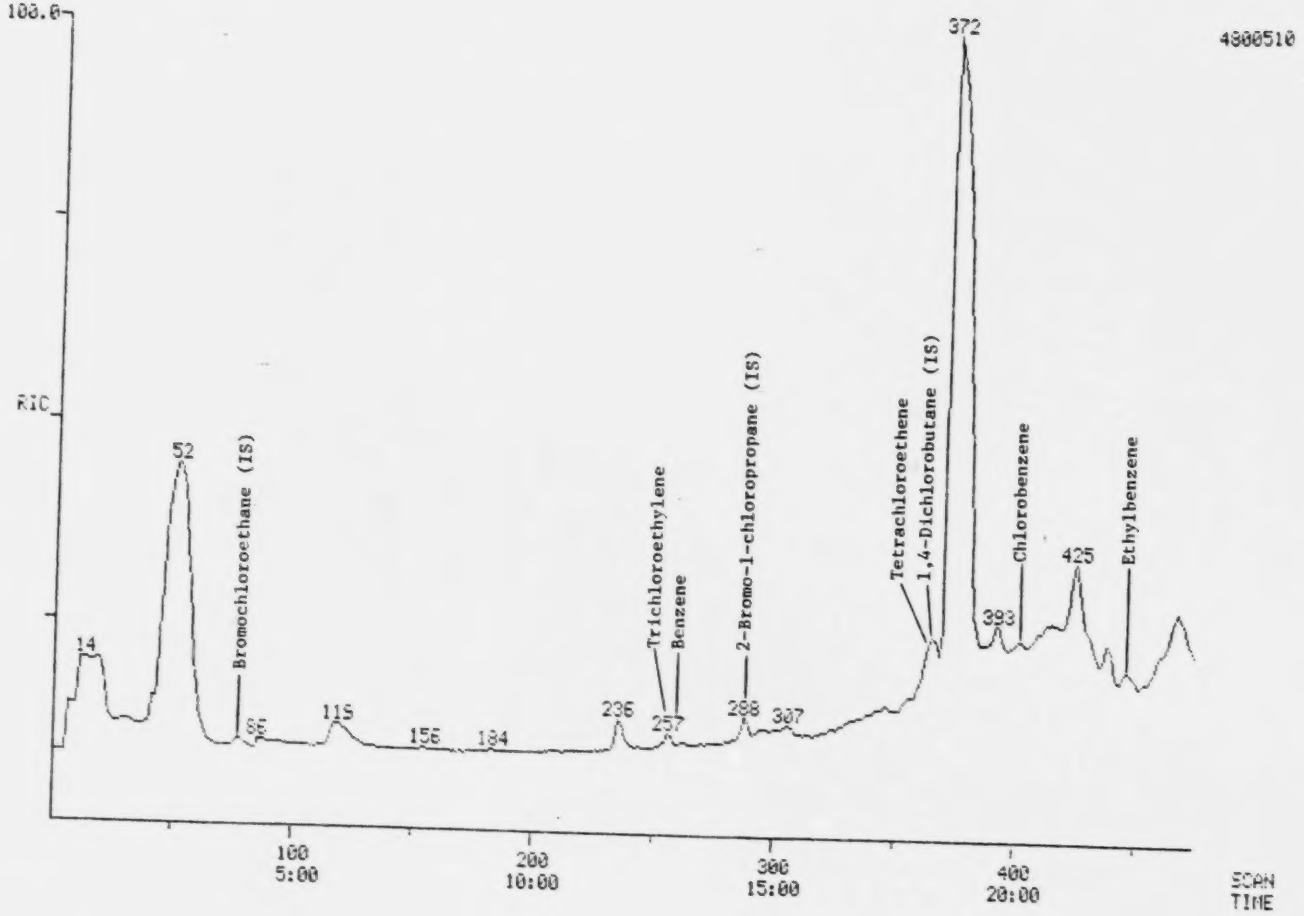

Figure 10. GC/MS chromatogram of a 5-ml aliquot of unspiked primary sludge analyzed with a stirred bottom frit tube.

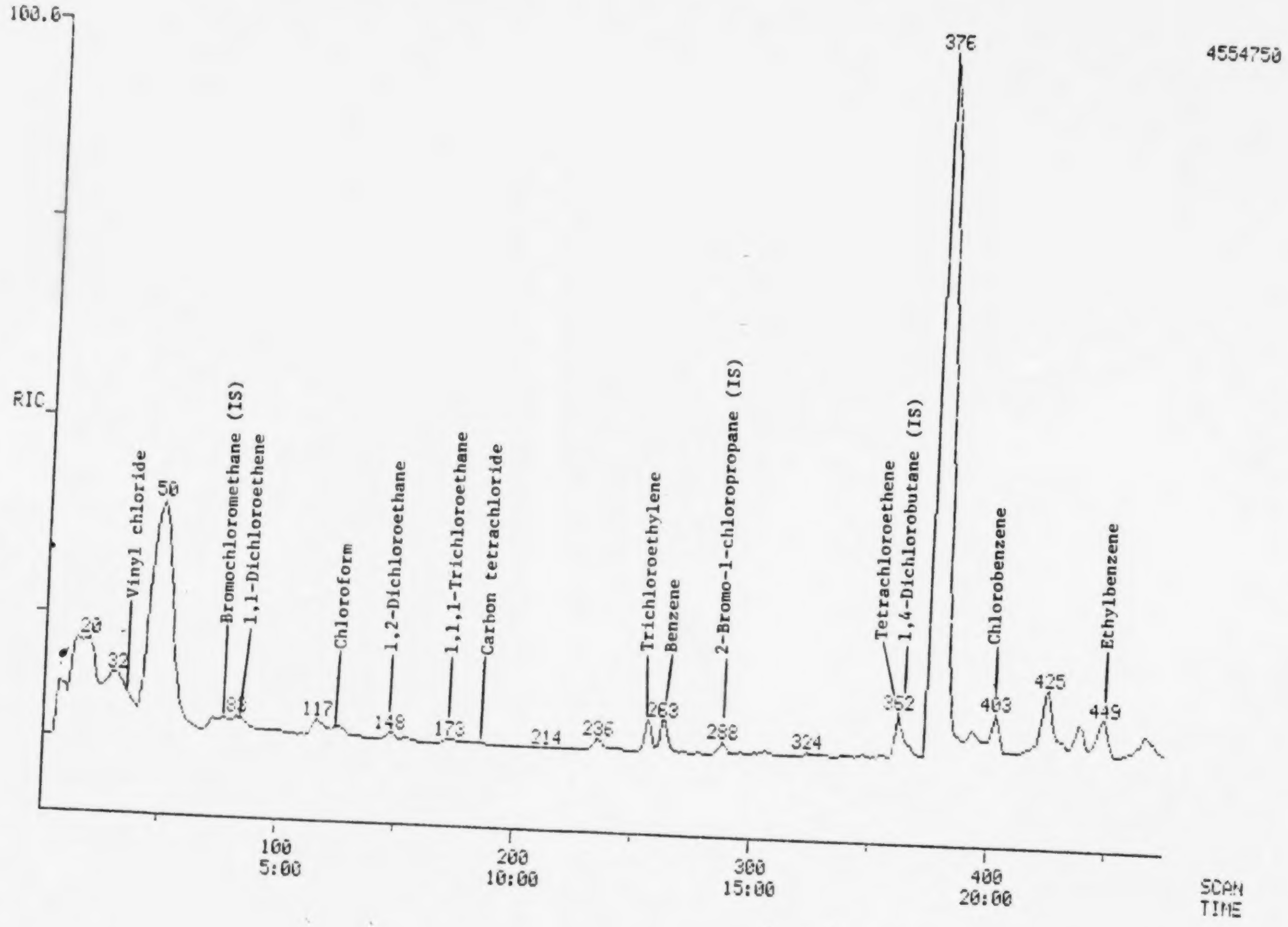

Figure 11. GC/MS chromatogram of a 5-ml aliquot of spiked primary sludge analyzed with a stirred bottom frit tube.

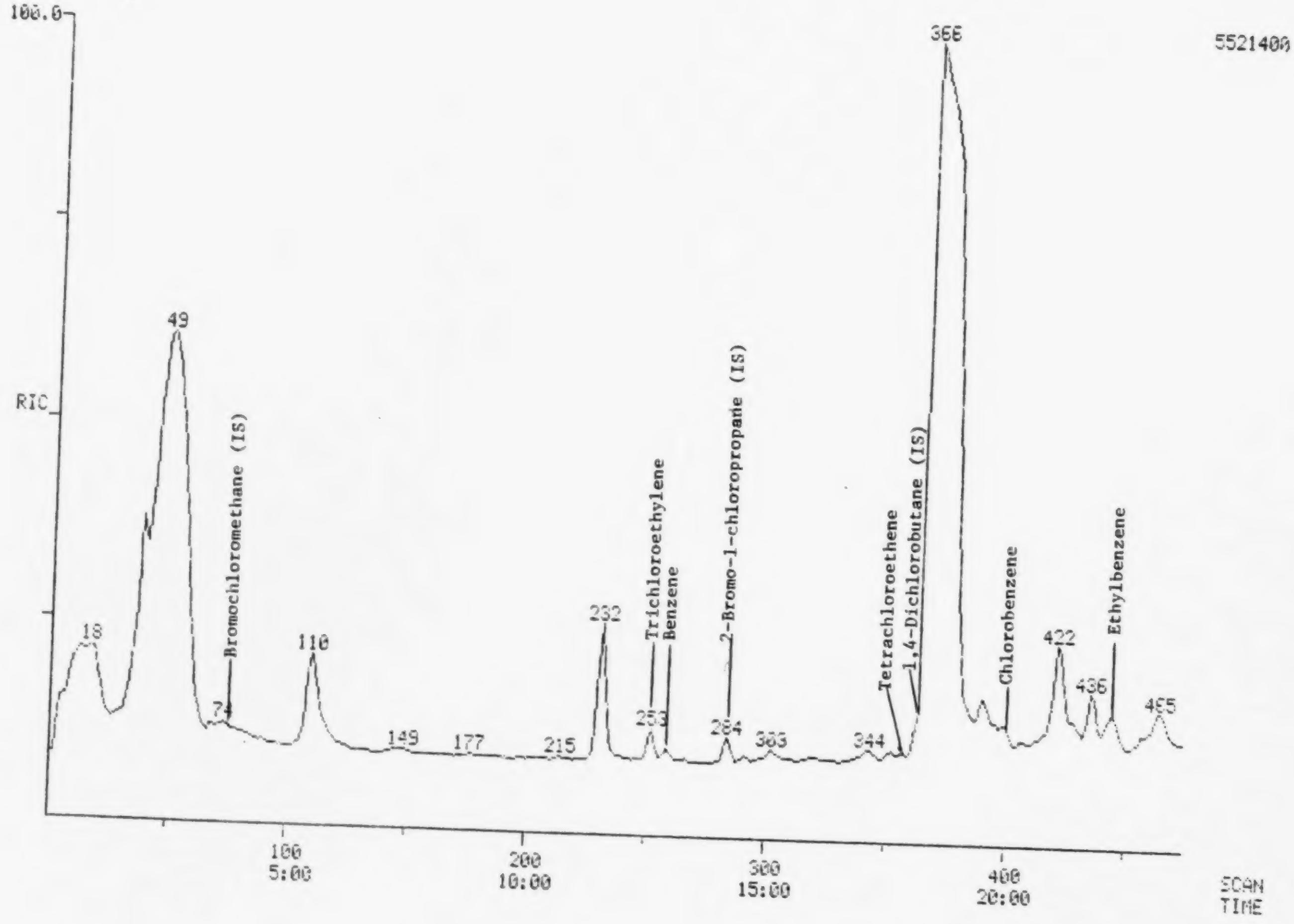

Figure 12. GC/MS chromatogram of a 10-ml aliquot of unspiked primary sludge analyzed with a stirred bottom frit tube.

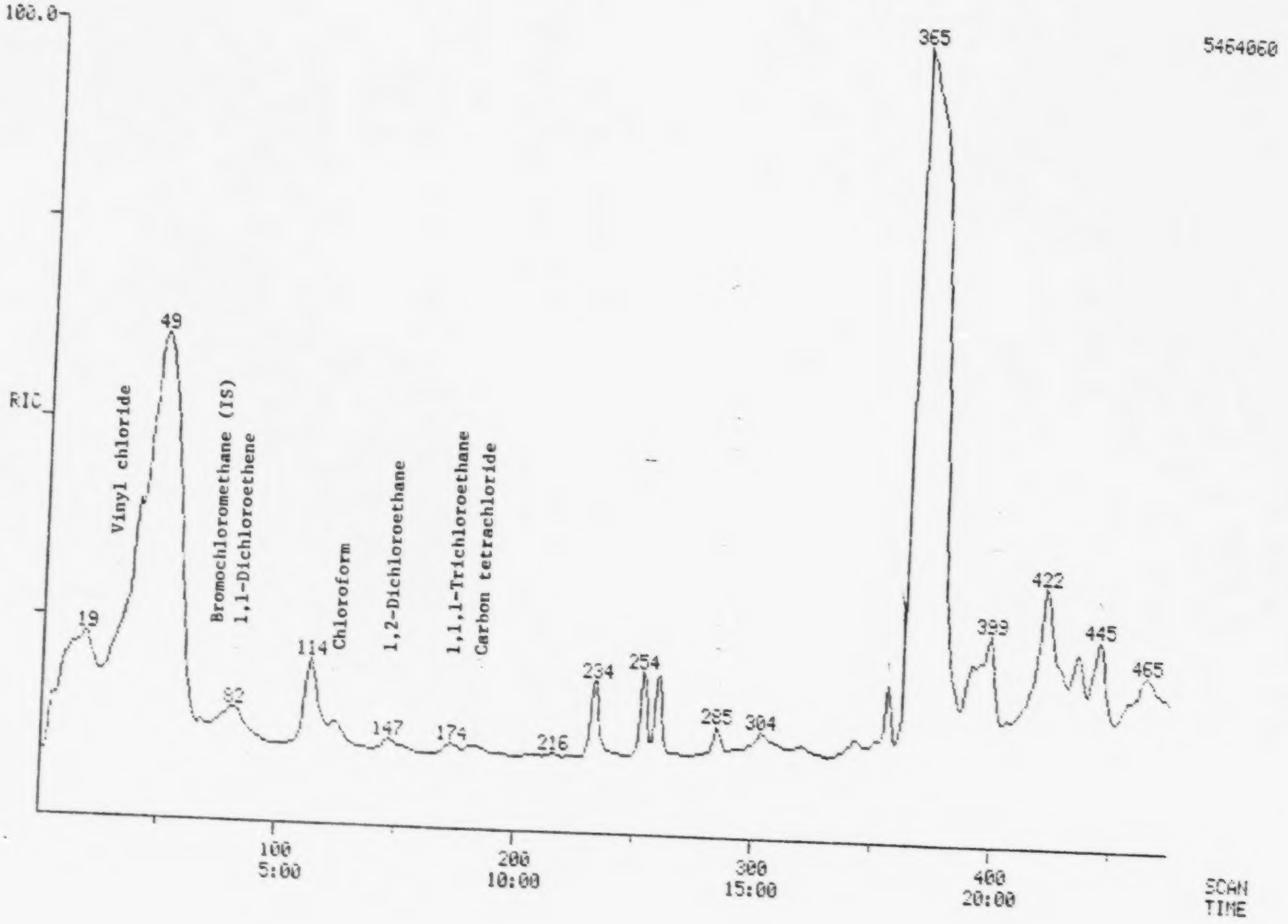

Figure 13. GC/MS chromatogram of a 10-ml aliquot of spiked primary sludge analyzed with a stirred bottom frit tube.

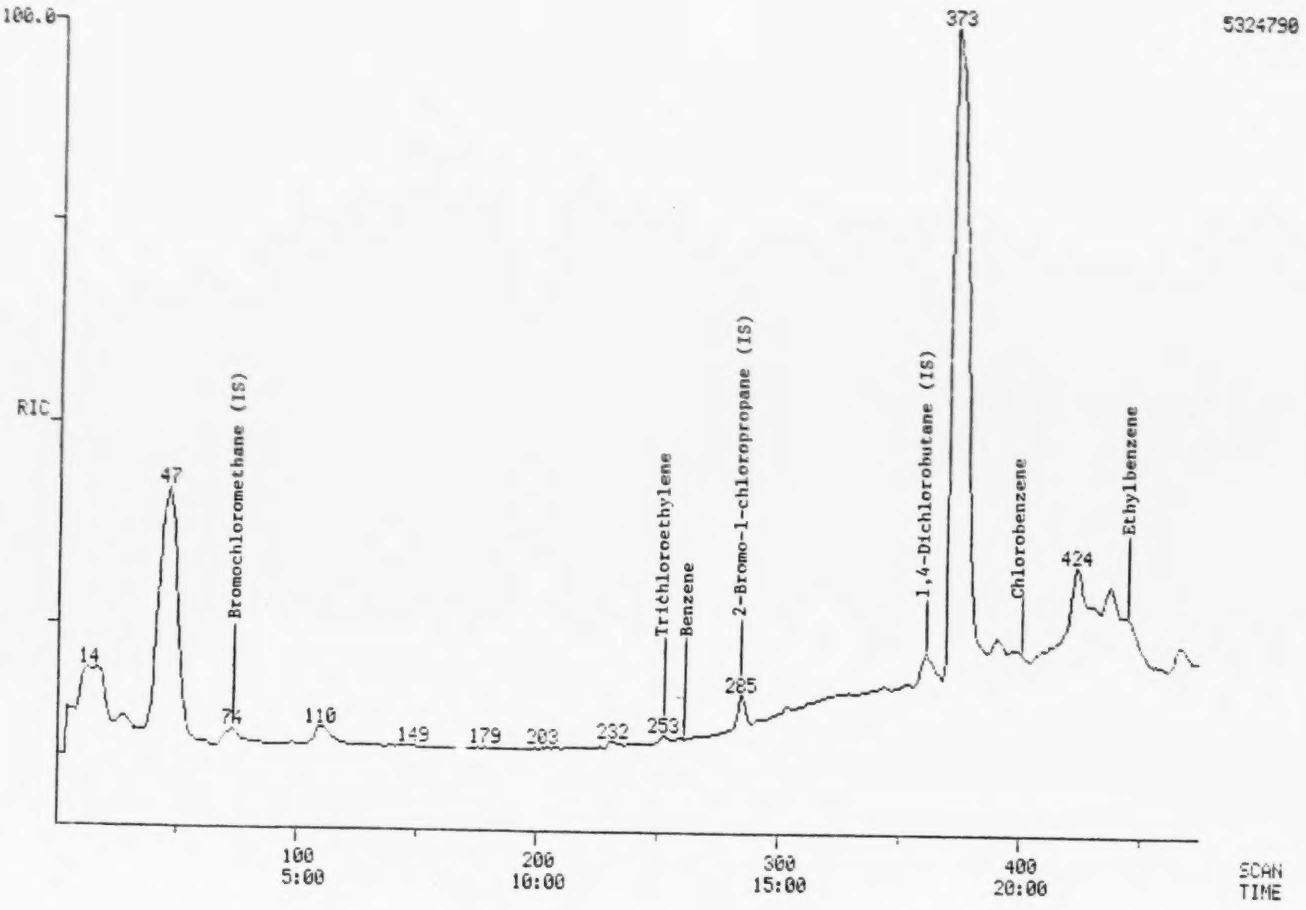

Figure 14. GC/MS chromatogram of a 2-ml aliquot of unspiked primary sludge analyzed with a conventional purge tube.

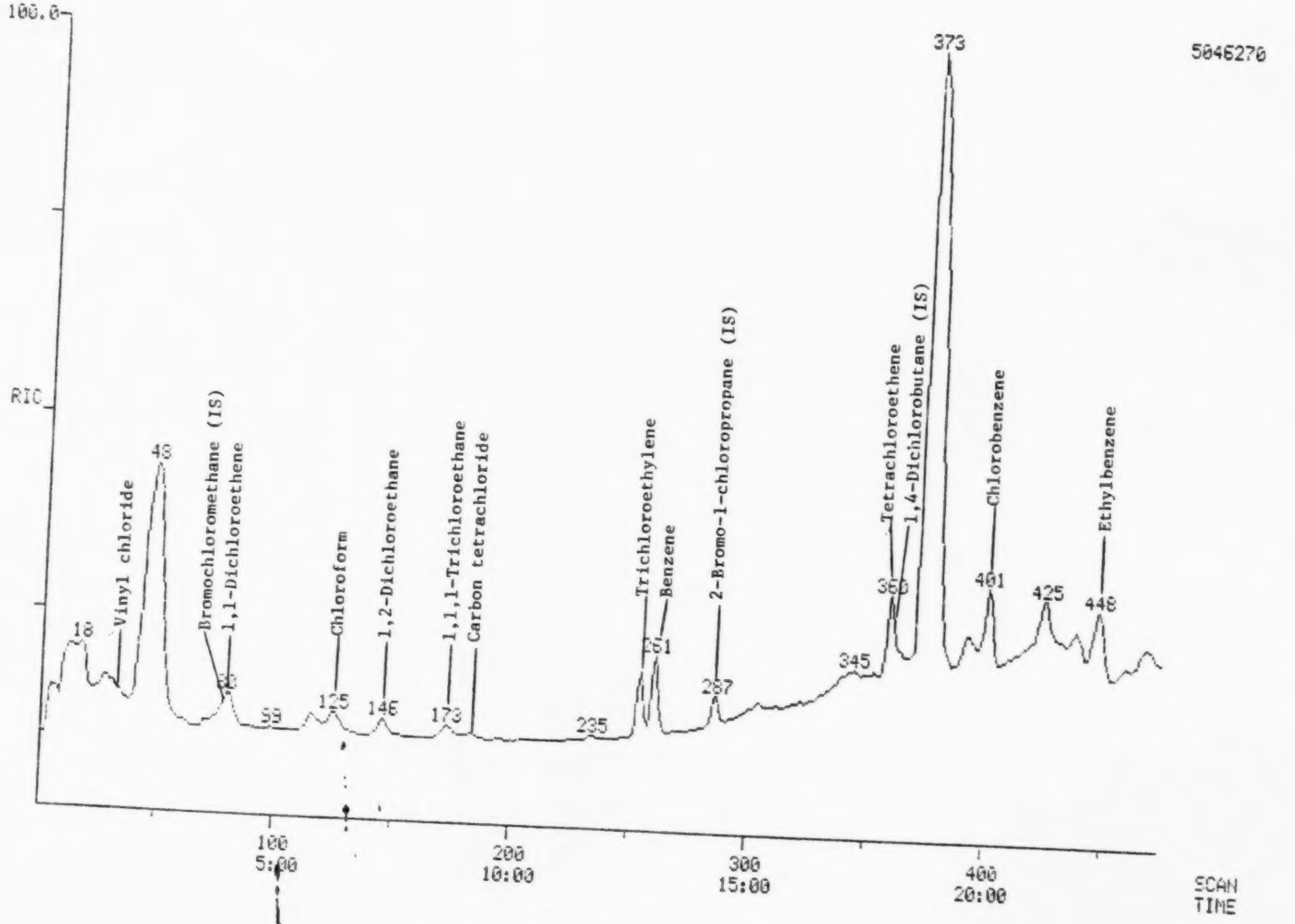

Figure 15. GC/MS chromatogram of a 2-ml aliquot of spiked primary sludge analyzed with a conventional purge tube.

EVALUATION OF THE PRECISION AND ACCURACY OF THE PURGEABLES PROTOCOL

The precision and accuracy of the purgeables protocol were evaluated by determining recoveries for spiked compounds from five primary sludges. The subject sludges, three from POTWs receiving various fractions of wastewater from residential and industrial sources and two from plants treating industrial wastewaters, were selected to provide a wide variety of sludge characteristics with which to test the performance of the method. The origin and characteristics of the five sludges are listed in Table 18. Recoveries were determined for the purgeable spiking compounds (listed in Table 1) fortified into these aliquot sludges at three levels. The spiking levels were chosen to be 2, 20, and 200 times the individual detection limit typically observed for each compound in sludge.

Experimental

Aliquots for each of the five sludge samples were prepared by filling 40.0-ml screw cap vials containing five small stainless steel balls and sealing the vials with no headspace with TFE-lined septa. Three sets of triplicate vials were spiked with the purgeables spiking compounds at 2, 20, and 200 times, respectively, the typical detection limits. Analytical standards were prepared at the same time by spiking 40.0-ml vials containing purgeables-free water with the same spiking solutions. All vials were allowed to equilibrate prior to analysis by tumbling at 4°C overnight. Each spiked and unspiked sludge sample was analyzed in triplicate by the purge-trap GC/MS methods described in the purgeables protocol (Method Appendix). In order to ensure that the responses for all compounds were observed within the working range of the mass spectrometric detector, only 2.0-ml aliquots were analyzed for the sludge aliquots spiked at 200 times the detection limit.

Results and Discussion

The recoveries determined for purgeable compounds spiked into the five primary sludge samples are summarized in Table 19. GC/MS chromatograms for unspiked and spiked Industrial No. 1 sludge are shown in Figures 16 to 19. Chromatograms for unspiked sludges from the remaining four plants are shown in Figures 20 to 23. Although the recoveries observed were generally good, many recovery determinations were likely influenced by relatively high concentrations of the spiking compounds in the unspiked sludges. Several compounds were present in some of the sludges at levels greater than the spike level, and in some cases concentrations in the unspiked sludges were more than 10 times the spike level. Recoveries for the latter cases were not representative of the method precision and accuracy and were excluded from the table. Zero or very low recoveries were observed for carbon tetrachloride in all sludges except Industrial No. 2. Although the detection limit for the spiking compounds were chosen based on considerable previous work, the detection limit for carbon tetrachloride in these particular sludges was evidently higher than is typical. The generally better recoveries and standard deviations observed from Industrial No. 2 may be related to its lower solids content. Determinations of vinyl chloride, chlorobenzene, and 1,1,1-trichloroethane were frequently obscured by coeluting interferences in the POTW sludges.

TABLE 18. PRIMARY WASTEWATER TREATMENT SLUDGES USED IN THE SLUDGE PROTOCOL PRECISION AND ACCURACY SPIKING STUDY

Plant	Location	Principal waste water inputs	% Solids in primary sludge
Platte Co. POTW	Suburban Kansas City, Missouri	Essentially 100% residential	3.0
Blue River POTW	Kansas City, Missouri	Residential and pretreated industrial	7.7
Kansas City, Kansas	Kansas City, Kansas	Largely industrial	9.5
Industrial No. 1	Southern United States	Petrochemical manufacturing	1.9
Industrial No. 2	Eastern United States	Various small industrial concerns	0.2[a]

[a] This sludge was prepared by dilution from a sludge fitter cake containing 37% solids.

TABLE 19. RESULTS OF PRECISION AND ACCURACY EVALUATIONS FOR THE PURGEABLES METHOD APPLIED TO MUNICIPAL AND INDUSTRIAL WASTEWATER TREATMENT PRIMARY SLUDGES

		Platte County POTW		Blue River POTW		Kansas City, Kansas, POTW		Industrial No. 1		Industrial No. 2	
Compound	Spike conc. (μg/L)	Unspiked conc. (μg/L)	Recovery (%)	Unspiked conc. (μg/L)	Recovery (%)	Unspiked conc. (μg/L)	Recovery (%)	Unspiked conc. (μg/L)	Recovery (%)	Unspiked conc. (μg/L)	Recovery (%)
Benzene	1	3 ± 1^{a}	97 ± 20^{a}	4 ± 0.8	230 ± 320^{b}	6 ± 6	290 ± 80^{b}	0.7 ± 0.3	93 ± 25	16 ± 0.1	c
	10		150 ± 30		250 ± 50		170 ± 29		118 ± 22		66 ± 9^{b}
	100^{d}		120 ± 15		140 ± 20		150 ± 8		114 ± 23		97 ± 3
Carbon tetrachloride	10	ND^{e}	0	ND	0	ND	0	ND	0	252 ± 14	c
	100		11 ± 4		0		0		0		85 ± 9^{b}
	1,000		0		0		0		0		87 ± 5
Chloroform	2	0.3 ± 0.3	120 ± 60	ND	0	ND	0	8 ± 0.4	80 ± 43^{b}	14 ± 0.6	82 ± 13^{b}
	20		130 ± 15		170 ± 39		47 ± 7		52 ± 16		81 ± 19
	200		62 ± 7		160 ± 23		110 ± 16		77 ± 17		82 ± 5
1,1-Dichloroethene	5	0.3 ± 0.5	200 ± 27	ND	260 ± 57	ND	170 ± 30	ND	130 ± 31	33 ± 3	0^{b}
	50		180 ± 26		200 ± 34		150 ± 24		160 ± 30		34 ± 24
	500		130 ± 15		130 ± 18		100 ± 10		130 ± 25		95 ± 5
Tetrachloroethene	3	1 ± 0.5	160 ± 56	89 ± 10	c	200 ± 52	c	ND	170 ± 65	880 ± 110	c
	30		180 ± 22		150 ± 42^{b}		29 ± 50^{e}		170 ± 50		c
	300		127 ± 4		140 ± 29		140 ± 13		200 ± 39		52 ± 5^{b}
Vinyl chloride	5	ND	f	f	f	ND	f	ND	120 ± 34	ND	0
	50		160 ± 39		170 ± 42		100 ± 12		160 ± 19		76 ± 10
	500		130 ± 16		100 ± 9		92 ± 2		140 ± 24		91 ± 8

(continued)

TABLE 19 (concluded)

		Platte County POTW		Blue River POTW		Kansas City, Kansas, POTW		Industrial No. 1		Industrial No. 2	
Compound	Spike conc. (μg/L)	Unspiked conc. (μg/L)	Recovery (%)	Unspiked conc. (μg/L)	Recovery (%)	Unspiked conc. (μg/L)	Recovery (%)	Unspiked conc. (μg/L)	Recovery (%)	Unspiked conc. (μg/L)	Recovery (%)
1,2-Dichloroethane	5	ND	140 ± 9	ND	240 ± 57	ND	150 ± 26	ND	81 ± 22	660 ± 110	c
	50		120 ± 18		170 ± 57		87 ± 5		130 ± 22		c
	500		130 ± 8		110 ± 18		95 ± 4		130 ± 18		86 ± 6[b]
Trichloroethene	2	165 ± 33		65 ± 11	c	13 ± 2	c	ND	170 ± 35	130 ± 8	c
	20		130 ± 61		280 ± 90		150 ± 40		160 ± 50		67 ± 44[b]
	200		110 ± 13		149 ± 29		140 ± 12		160 ± 39		92 ± 6
1,1,1-Trichloroethane	16	2 ± 3	140 ± 29	ND	91 ± 50	ND	f	ND	110 ± 17	1,240 ± 52	c
	160		120 ± 28		190 ± 57		91 ± 13		180 ± 31		67 ± 13[b]
	1,600		130 ± 13		170 ± 40		120 ± 12		110 ± 5		100 ± 7
Chlorobenzene	2	0.4 ± 0.4	150 ± 60	ND	f	f	f	ND	250 ± 33	13 ± 0.5	85 ± 10
	20		160 ± 11		120 ± 19		66 ± 7		160 ± 40		110 ± 6
	200		120 ± 7		120 ± 31		130 ± 9		180 ± 40		97 ± 5
Ethylbenzene	5	4 ± 2	100 ± 33	38 ± 2	160 ± 150	69 ± 24	c	1 ± 0.4	180 ± 21	1,090 ± 190	c
	50		150 ± 6		110 ± 33		47 ± 26[b]		190 ± 44		88 ± 21[c]
	500		100 ± 8		120 ± 27		110 ± 9		140 ± 16		70 ± 7[b]

a Mean ± standard deviation for three determinations.

b Concentration determined in the unspiked sludge was higher than the spike level.

c Concentration determined in the unspiked sludge was 10 times higher than the spike level.

d Analyzed from a 2-ml aliquot diluted to 10 ml prior to purging.

e ND = not detected.

f Determination was not possible because of the presence of coeluting interferences.

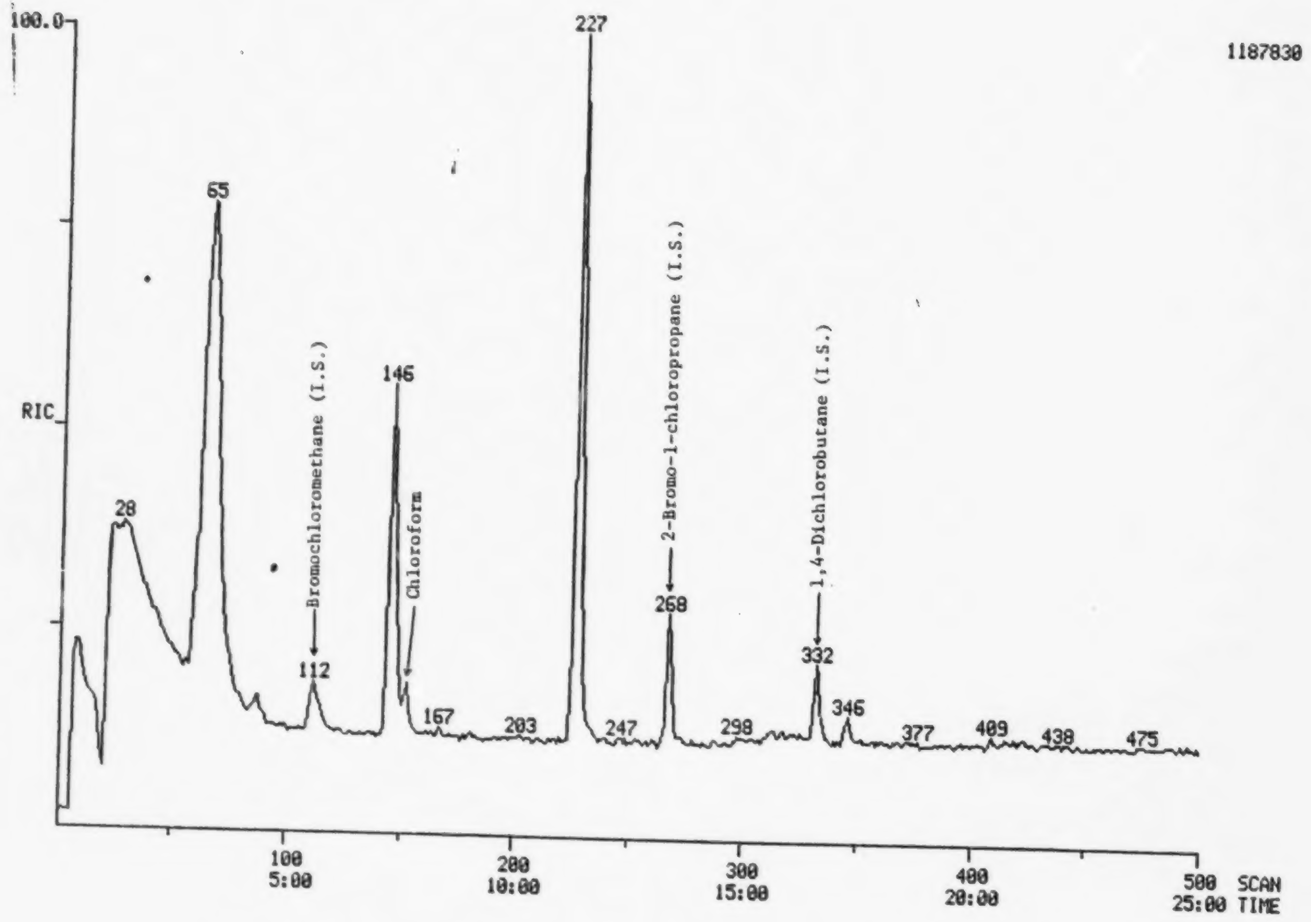

Figure 16. GC/MS chromatogram for purgeables in unspiked Industrial No. 1 primary sludge.

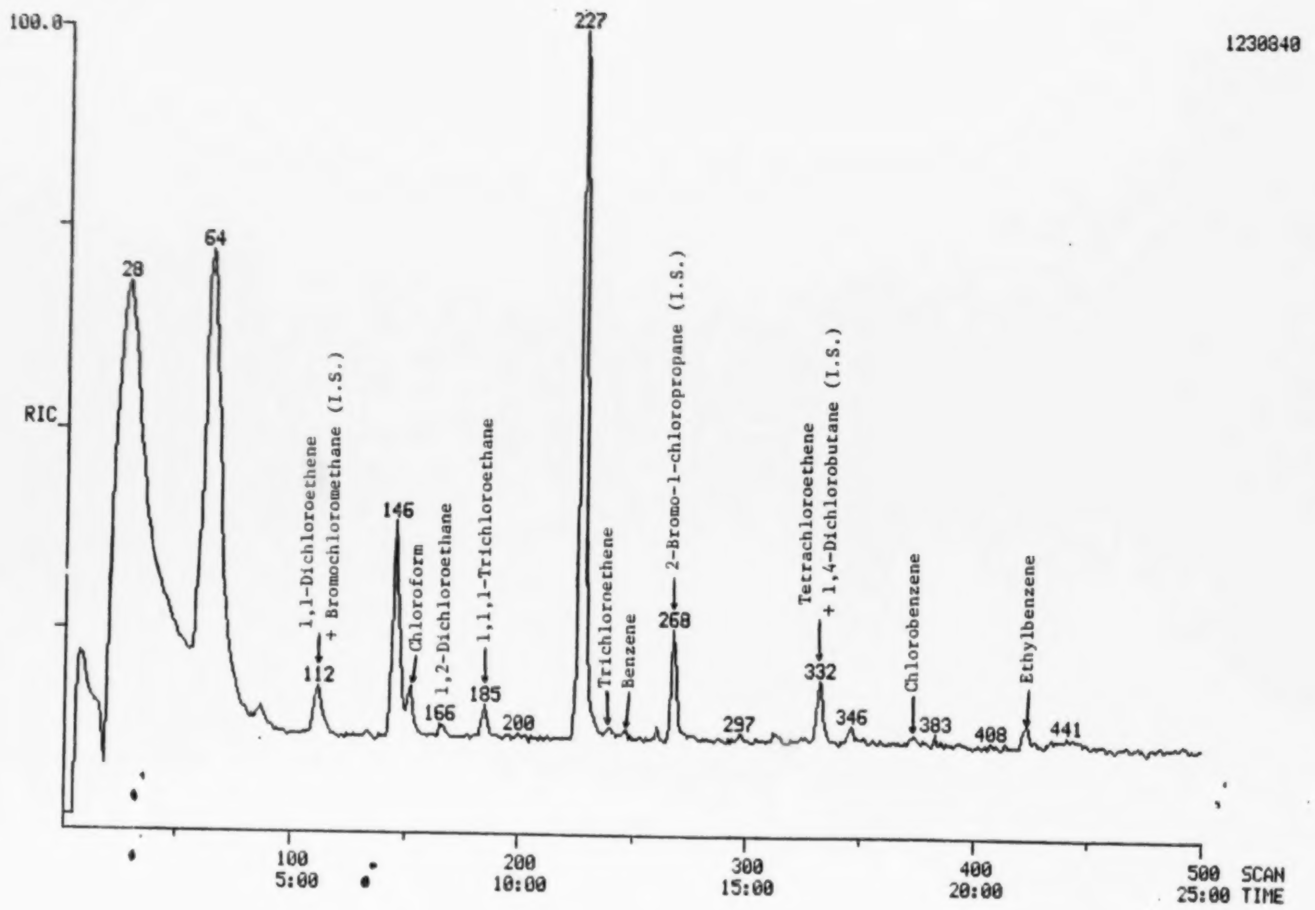

Figure 17. GC/MS chromatogram for purgeables in Industrial No. 1 primary sludge spiked at two times the detection limits for selected compounds.

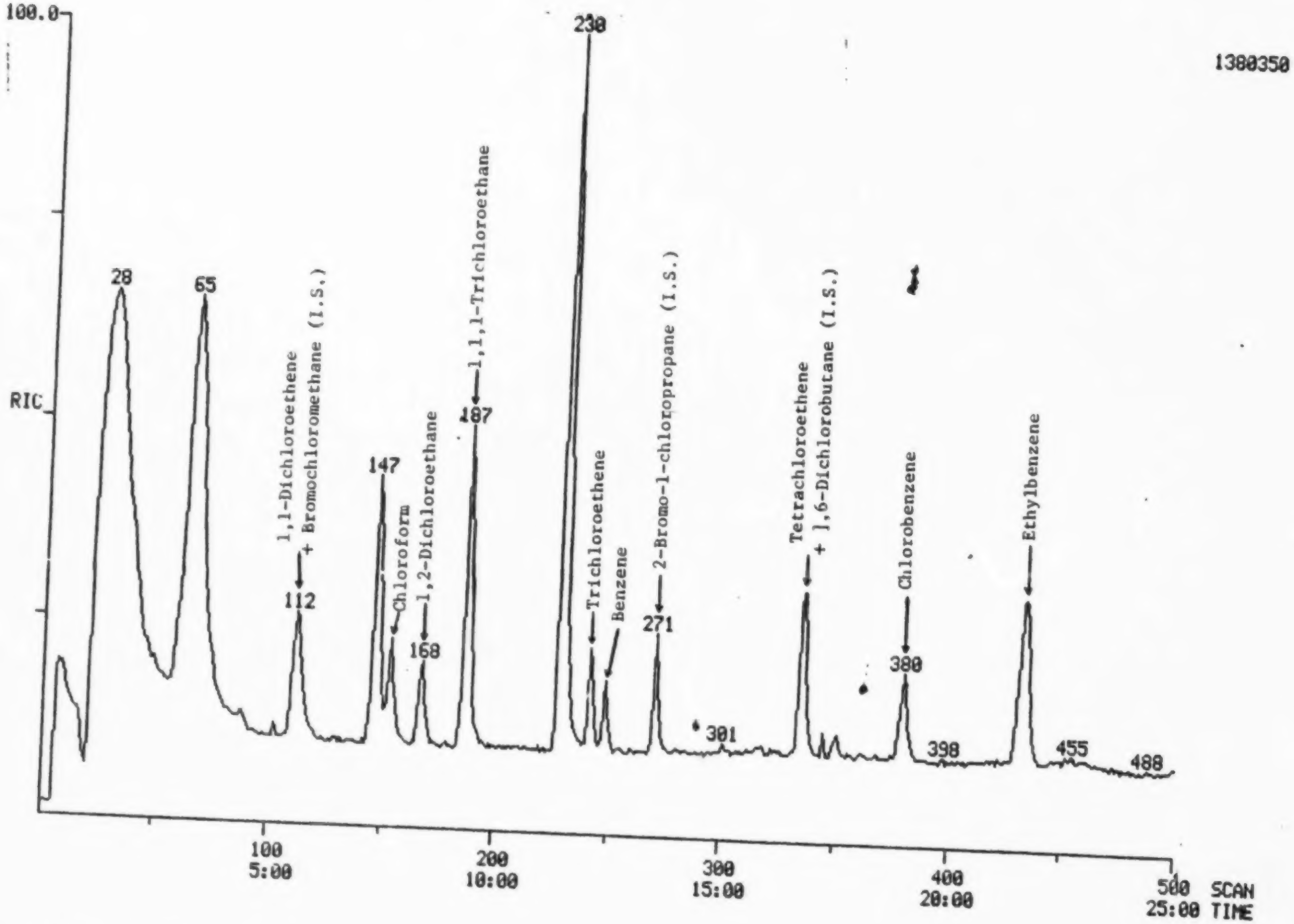

Figure 18. GC/MS chromatogram for purgeables in Industrial No. 1 primary sludge spiked at 20 times the detection limits for selected compounds.

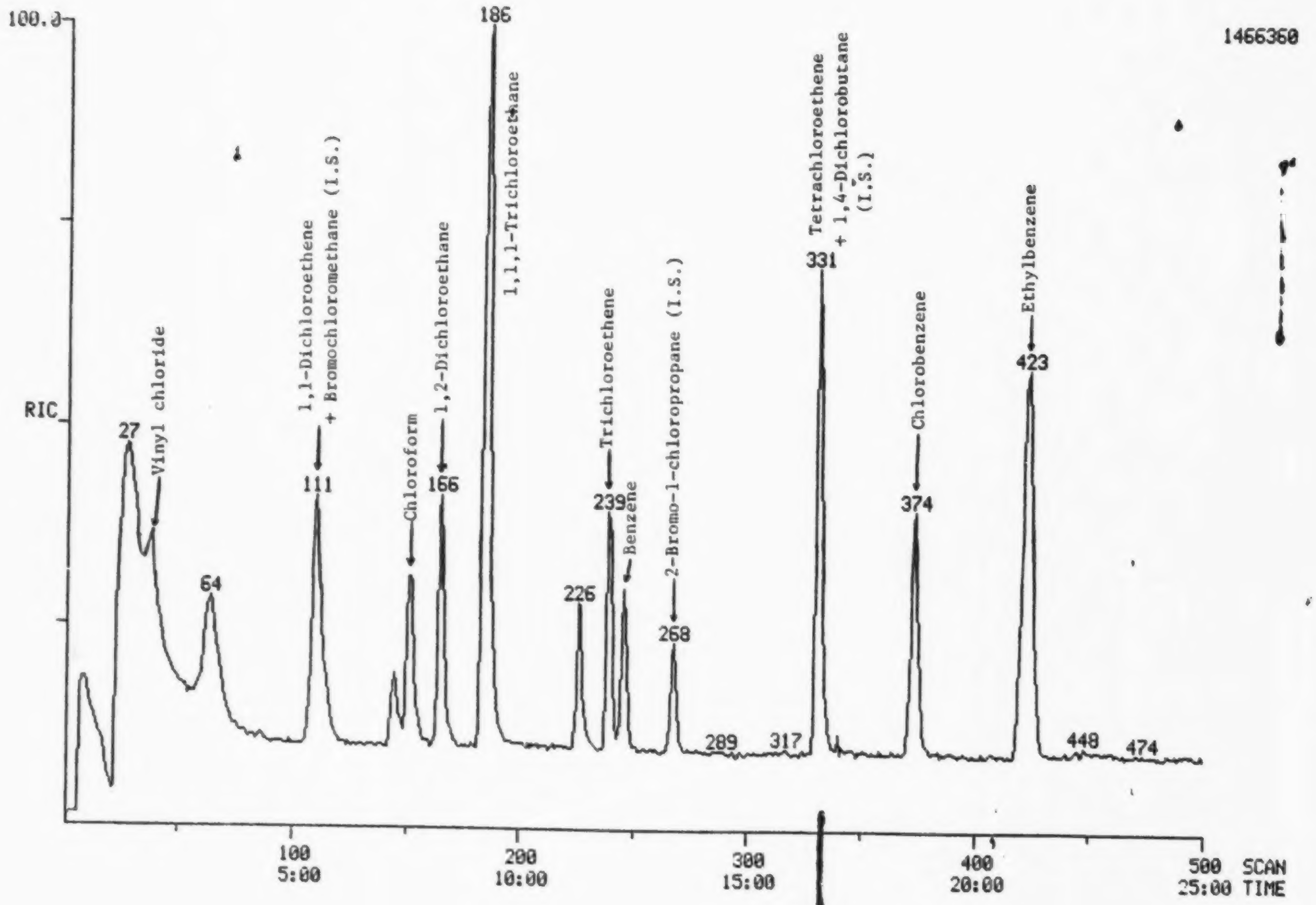

Figure 19. GC/MS chromatogram for purgeables in Industrial No. 1 primary sludge spiked at 200 times the detection limits for selected compounds.

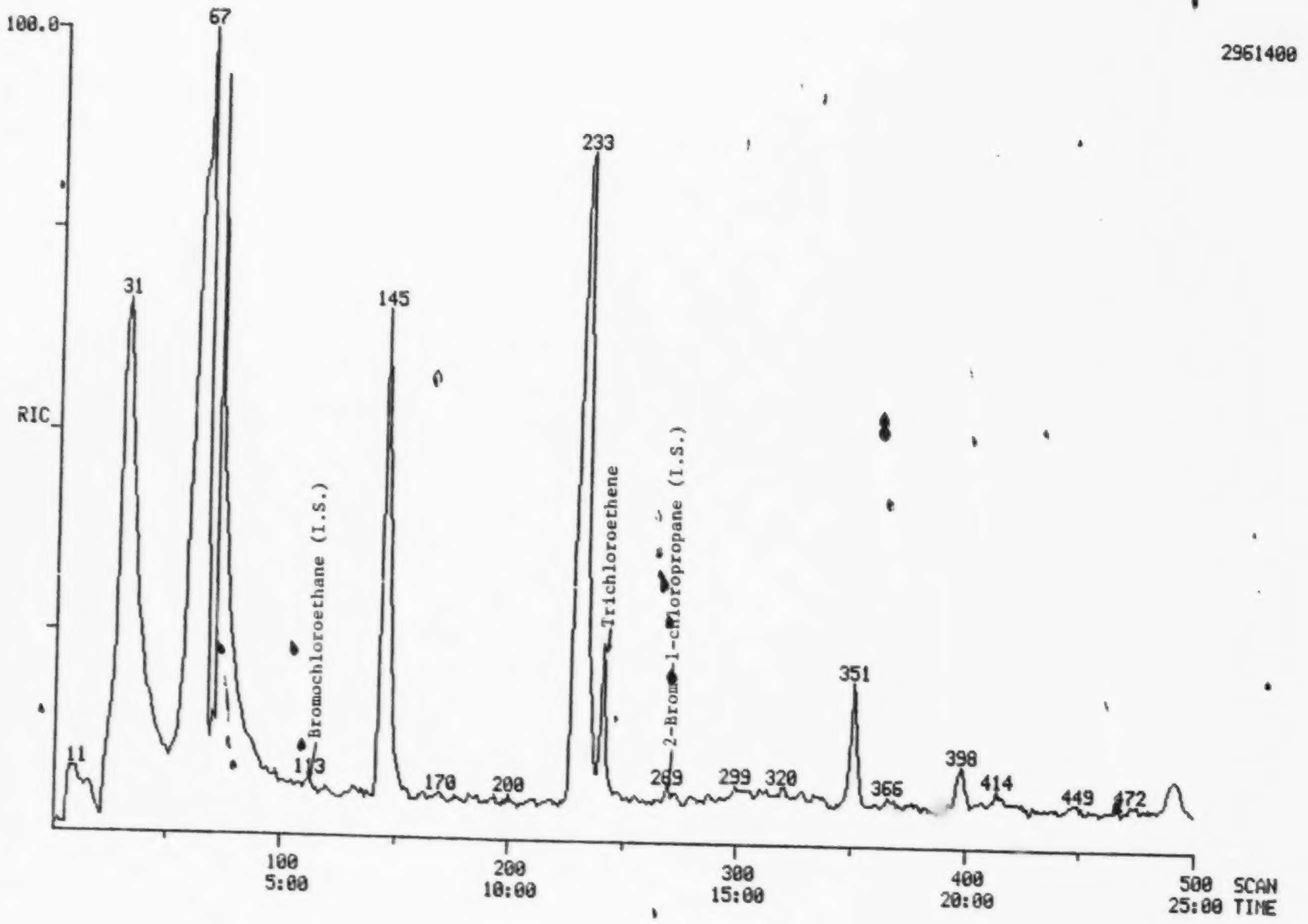

Figure 20. GC/MS chromatogram for purgeables in unspiked Platte County POTW primary sludge.

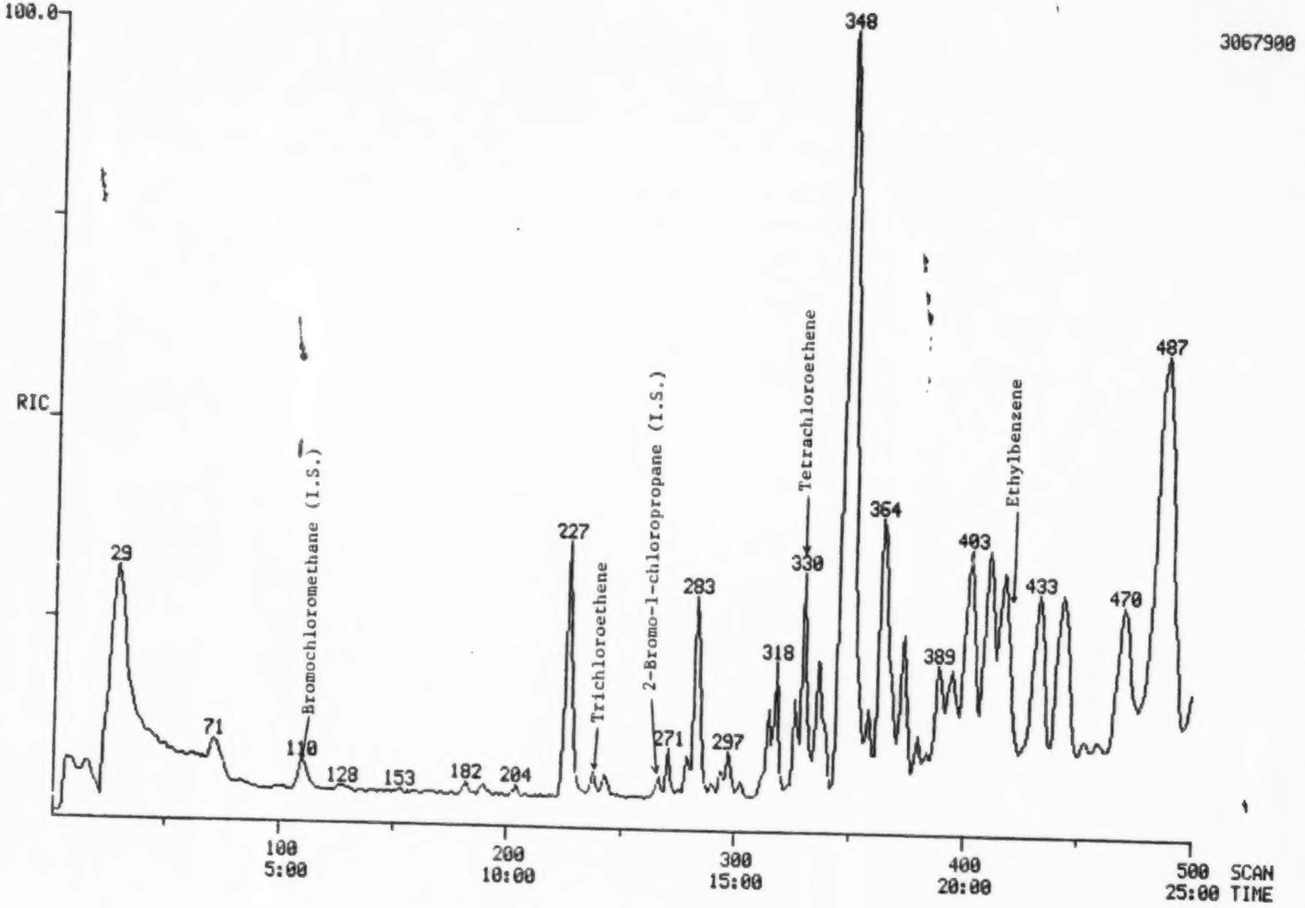

Figure 21. GC/MS chromatogram for purgeables in unspiked Blue River POTW primary sludge.

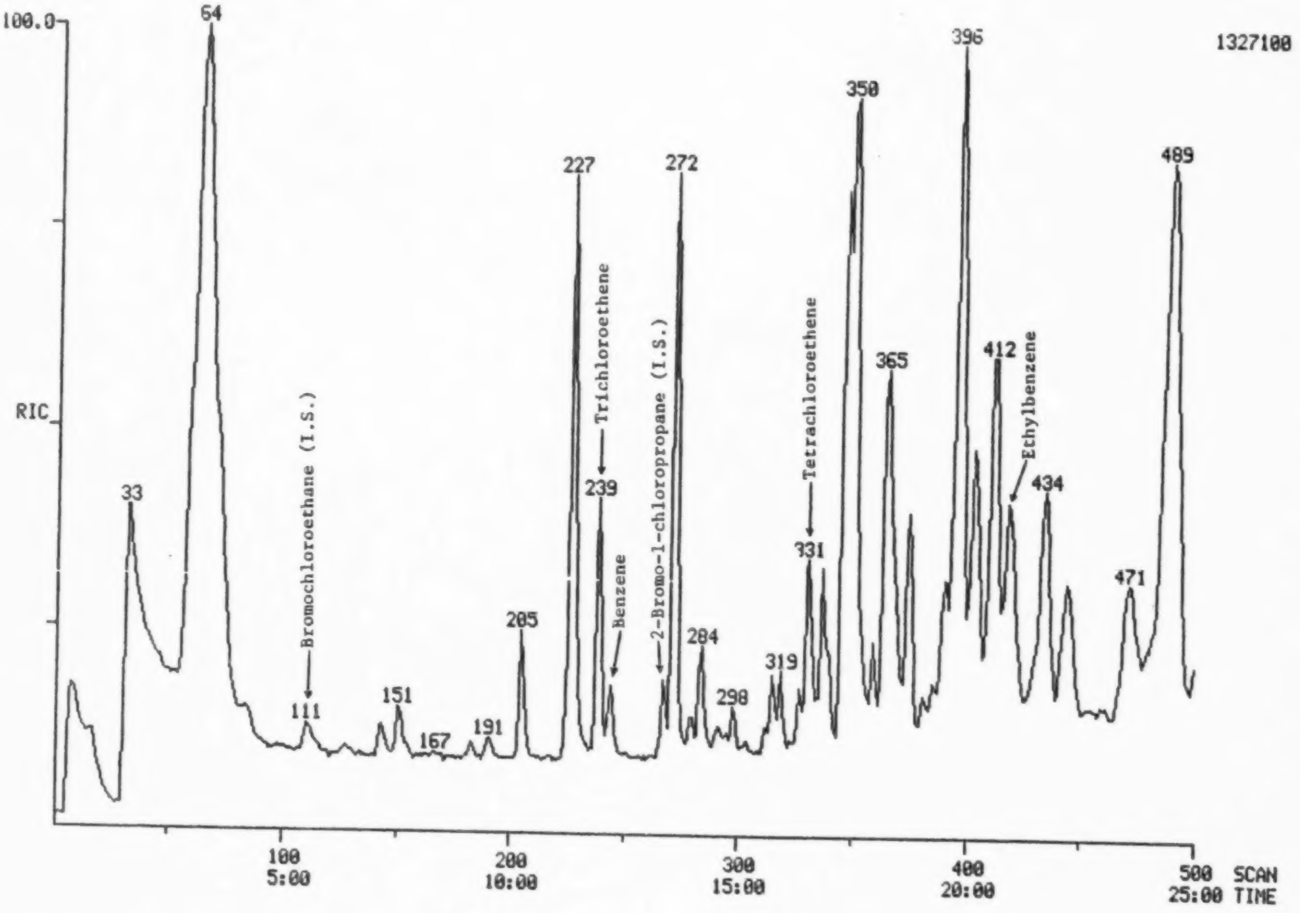

Figure 22. GC/MS chromatogram for purgeables in unspiked Kansas City, Kansas, POTW primary sludge.

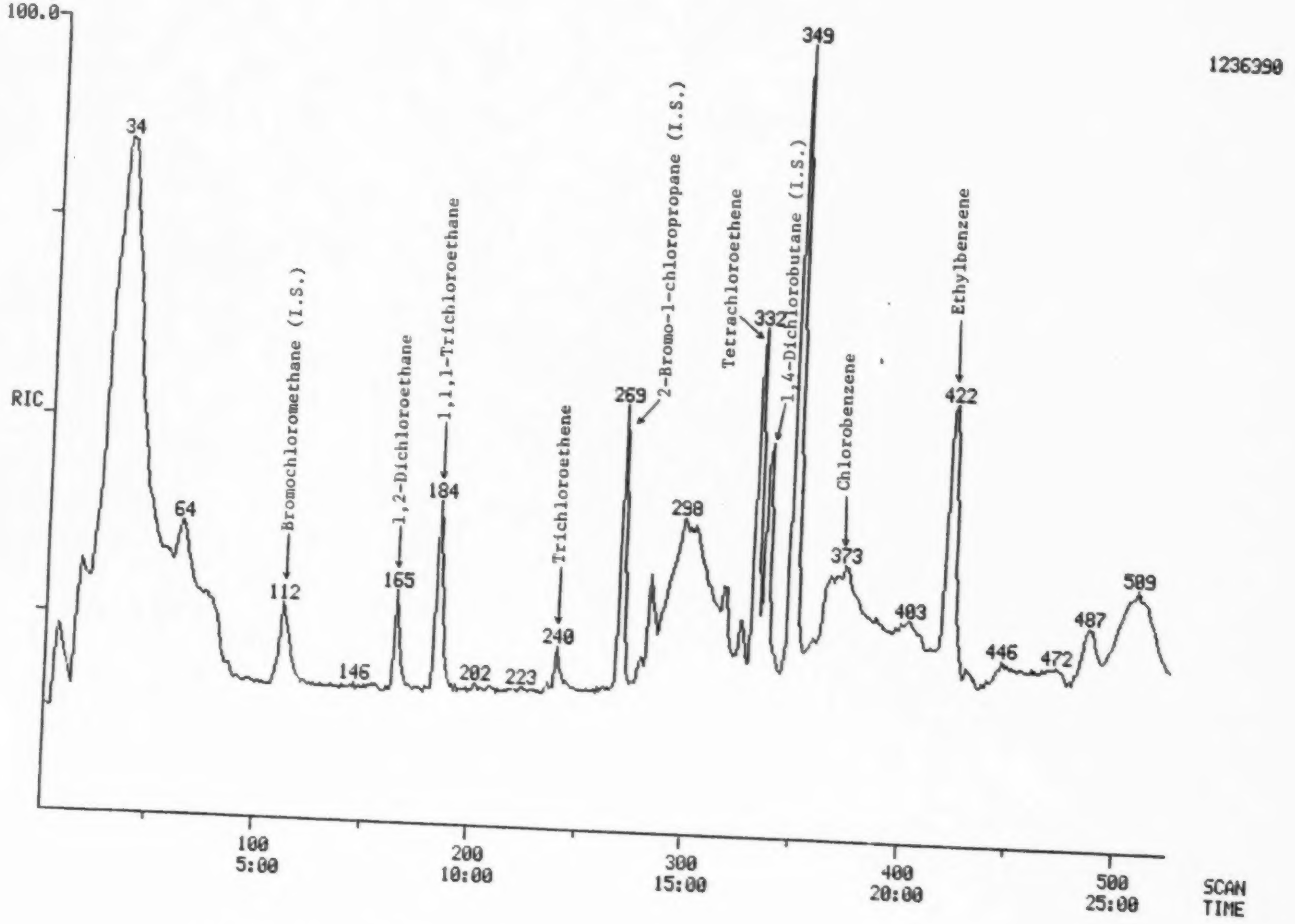

Figure 23. GC/MS chromatogram for purgeables in unspiked Industrial No. 2 primary sludge.

Nonetheless, in most cases the recoveries observed were both good and reproducible. Only 11% of all recovery determinations were less than 50%. More than 63% fell within the range of 50 to 150% recovery. An additional 25% of the recovery determinations exceeded 150%. Spike recoveries in excess of 100% may reflect slightly lower recoveries for the internal quantitation standards relative to the anaytes. The relative standard deviations (RSD) for triplicate recovery determinations were generally low. More than 90% of the RSDs were 30% or less. Of those, 27% were less than 10% RSD. The method reproducibility was surprisingly good considering the difficulty in removing representative aliquots from a heterogeneous sample matrix. Considering the variability of sludge characteristics, the heterogeneous nature of sludges, and the detection limits achieved, the results of these precision and accuracy determinations demonstrate that the proposed method can be reliably applied to the analysis of purgeable compounds in municipal and industrial wastewater treatment sludges.

TIME/COST ANALYSIS OF THE METHOD

In general, the per sample labor and costs required for analyses of sludge samples by the purge-trap GC/MS protocol (Method Appendix) are similar to those for wastewater analyses. However, the analysis of a higher percentage of spiked and duplicate samples may be required to check the precision and accuracy of the method for each sludge matrix. Estimates of the labor and cost were based on several important conditions:

* Analyses would be conducted by professional analytical chemists who are experienced in trace organic analysis of sludges or at least in trace organic analysis of difficult sample matrices.

* No major equipment would be purchased. Only the costs of replacing consumable supplies and glassware were estimated.

* Sample analyses would be conducted on lots of 20 to 100 samples. Analysis of fewer samples would result in higher per sample costs.

* Analytical standard solutions would be prepared from commercially available mixed standard solutions. Preparation of mixed analytical standards from the pure compounds requires a considerable labor investment that may not be cost-effective for sample lots of 100 or less.

Under these conditions, the per sample time/cost estimate for analysis of purgeables in sludge is 2.5 labor-hours of technical effort and direct supervision, 1.0 h of GC/MS instrument time, and $10 for other direct costs. Of the labor hours, 1.5 h are estimated for data retrieval, interpretation, and reporting.

Many operations associated with routine analysis of purgeables in sludges are dependent on the specific program objectives and are not included in these estimates. However, they do contribute to the overall cost of the program.

These operations include analysis of spiked and replicate samples for analytical quality control and miscellaneous sample handling such as preparing composite samples and spiking samples. In addition, reanalysis may be required for samples with analyte responses outside the dynamic range of the GC/MS detector. As many as 30 to 40% reruns are typically required for routine analysis of POTW sludges from various sources.[5]

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[5] Hansen, E. M., Midwest Research Institute, personal communication (1980).

SECTION 5

DEVELOPMENT AND EVALUATION OF METHODS FOR EXTRACTABLE COMPOUNDS

As was the case for purgeable compounds, the development of methods for the analysis of extractable compounds in sludge focused initially on adapting the EPA protocol for industrial wastewaters.[1] The differences in character between some untreated industrial and municipal wastewaters and many sludges are minimal. In general, sludges contain higher levels of both dissolved and suspended solids. The high solids content of sludges poses a significant barrier to efficient extraction of the acidic, basic, and neutral compounds. In addition, the high level of extractable materials in sludges necessitates the use of selective extract preparation methods to mitigate coextracted interferences. Development of efficient and selective extraction methods for sludges is a formidable challenge because of the wide range of physical and chemical properties of the organic priority pollutants. The initial approach to achieve these objectives was to develop an efficient but somewhat less selective extraction procedure followed by an extract cleanup procedure to remove interfering coextractants and produce an extract of sufficient quality for GC/MS analysis.

This section describes the development of a preliminary method for extractable compounds in POTW sludge based on relatively expedient adaptations of the wastewater screening protocol. Following the development of a workable preliminary method, several alternative extraction and extract cleanup procedures were investigated and a capillary GC/MS method was developed. The results of these experiments led to the development of a revised protocol for extractable compounds. The precision and accuracy of the revised method were evaluated for five samples of POTW and industrial wastewater treatment sludge, and the labor- and instrument-hours required for conducting analyses with this protocol were estimated.

DEVELOPMENT OF A PRELIMINARY PROTOCOL FOR POTW SLUDGE

Under the industrial wastewater protocol, wastewater samples are sequentially extracted with dichloromethane under basic and then acidic conditions. The base/neutral (B/N) and acid extracts are individually concentrated and analyzed by individual packed column GC/MS procedures. The B/N extract contains the benzidenes and neutral compounds and the acid extract contains the phenolic compounds. The analytical scheme for wastewaters is illustrated in Figure 24.

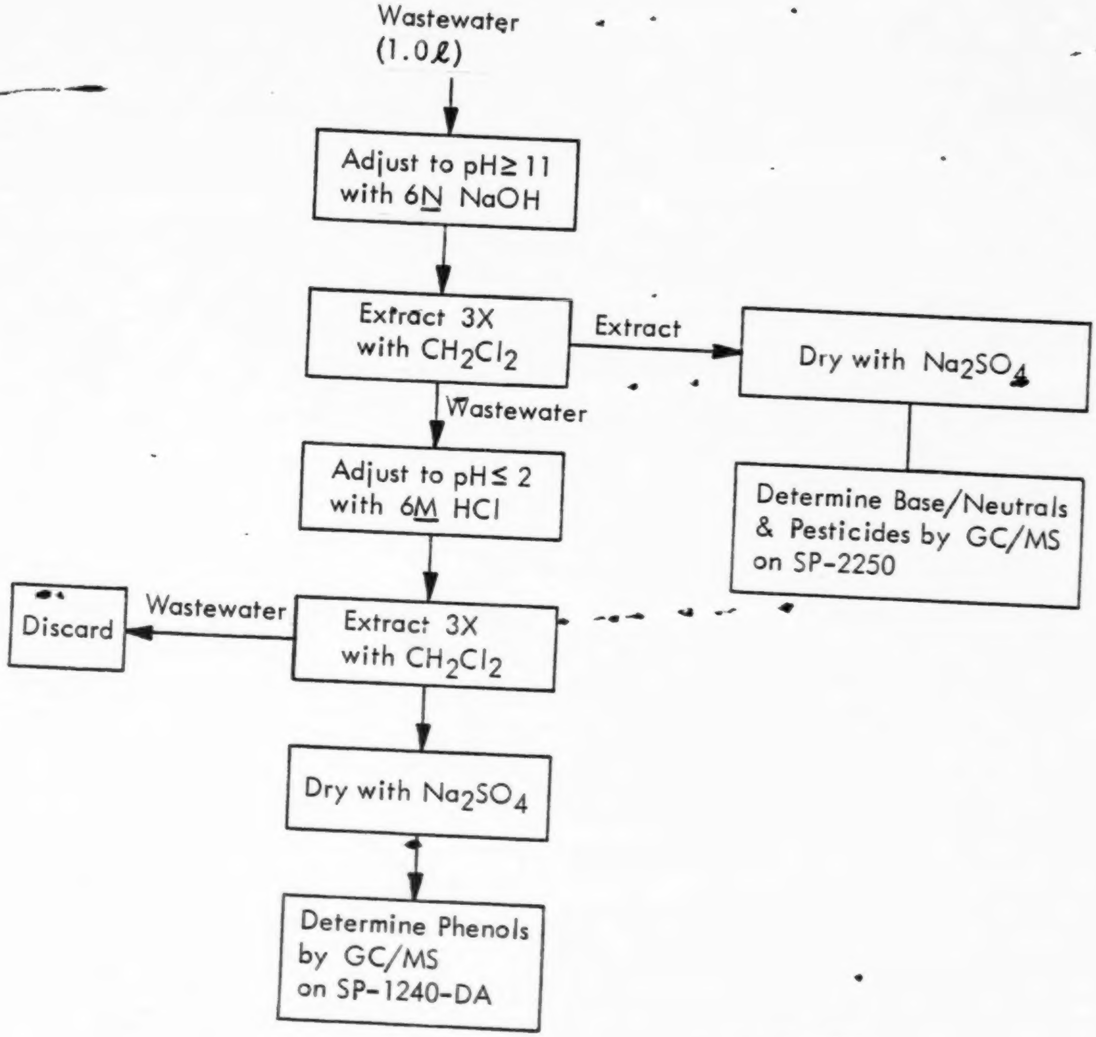
Wastewater
(1.0ℓ)
Adjust to pH≥ 11 with 6N NaOH
Extract 3X with CH_2Cl_2
Extract
Dry with Na_2SO_4
Wastewater
Determine Base/Neutrals & Pesticides by GC/MS on SP-2250
Adjust to pH≤ 2 with 6M HCl
Discard
Wastewater
Extract 3X with CH_2Cl_2
Dry with Na_2SO_4
Determine Phenols by GC/MS on SP-1240-DA

Figure 24. Analysis scheme for extractable compounds in industrial wastewater.

The performance of these GC/MS procedures for analyses of B/N and acidic compounds has been well demonstrated. Hence, the primary objective in adapting the wastewater methods was to develop procedures for sludge extraction and extract cleanup to provide extracts of sufficient quality for GC/MS analysis. Many of the extractable compounds were expected to strongly associate with the sludge solids. Hence, it was anticipated that the wastewater extraction method, i.e., simple liquid-liquid partitioning with dichloromethane, would not provide sufficient contact of the extracting solvent with the solids to allow efficient extraction of those compounds from sludges and would be hindered by formation of emulsions. A procedure using a high speed homogenizer probe to provide vigorous mixing and blending of the sludge aliquot with the extracting solvent was evaluated. The homogenized mixture was separated by centrifugation and the extract withdrawn with a pipette.

Unfortunately, this vigorous homogenization/centrifugation procedure also extracts large quantities of lipids, fatty acids, and other high molecular weight compounds present in POTW sludges. These compounds can cause significant interferences during GC/MS analysis and necessitate extract cleanup. A preparative scale, low pressure, gel permeation chromatography (GPC) procedure was selected for removing these high molecular weight materials from sludge extracts. GPC techniques have been successfully applied to the removal of lipid materials from fish extracts prepared for analysis of chlorinated pesticides.[6] Kloepfer and Bunn[7] modified the procedure used for pesticides in fish by developing a dichloromethane elution method for sludge extracts.

A scheme for the analysis of extractable compounds in sludge using basic then acidic homogenization/centrifugation extraction and GPC cleanup is illustrated in Figure 25. In an attempt to further simplify a preliminary method for extractable compounds, a single pH extraction scheme was proposed which would be based on the recoveries for selected basic, neutral, and acidic compounds from water at several pHs. Evaluations of the two proposed analytical schemes are described below.

Evaluation of a Dual pH Extraction Scheme

The dual pH (basic then acidic) extraction scheme was evaluated by determining recoveries for the extractable analytes spiked into primary and secondary sludge from the Belmont POTW (Indianapolis, Indiana) and combined sludge from the Muddy Creek POTW (Cincinnati, Ohio).

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[6] Stalling, D. L., R. C. Tindle and J. L. Johnson. Cleanup of Pesticides and Polychlorinated Biphenyl Residues in Fish Extracts by Gel Permeation Chromatography. JAOAC 55:32-38 (1972).

[7] Kloepfer, R. and W. Bunn, Region VII, Environmental Protection Agency Kansas City, personal communication (1979).

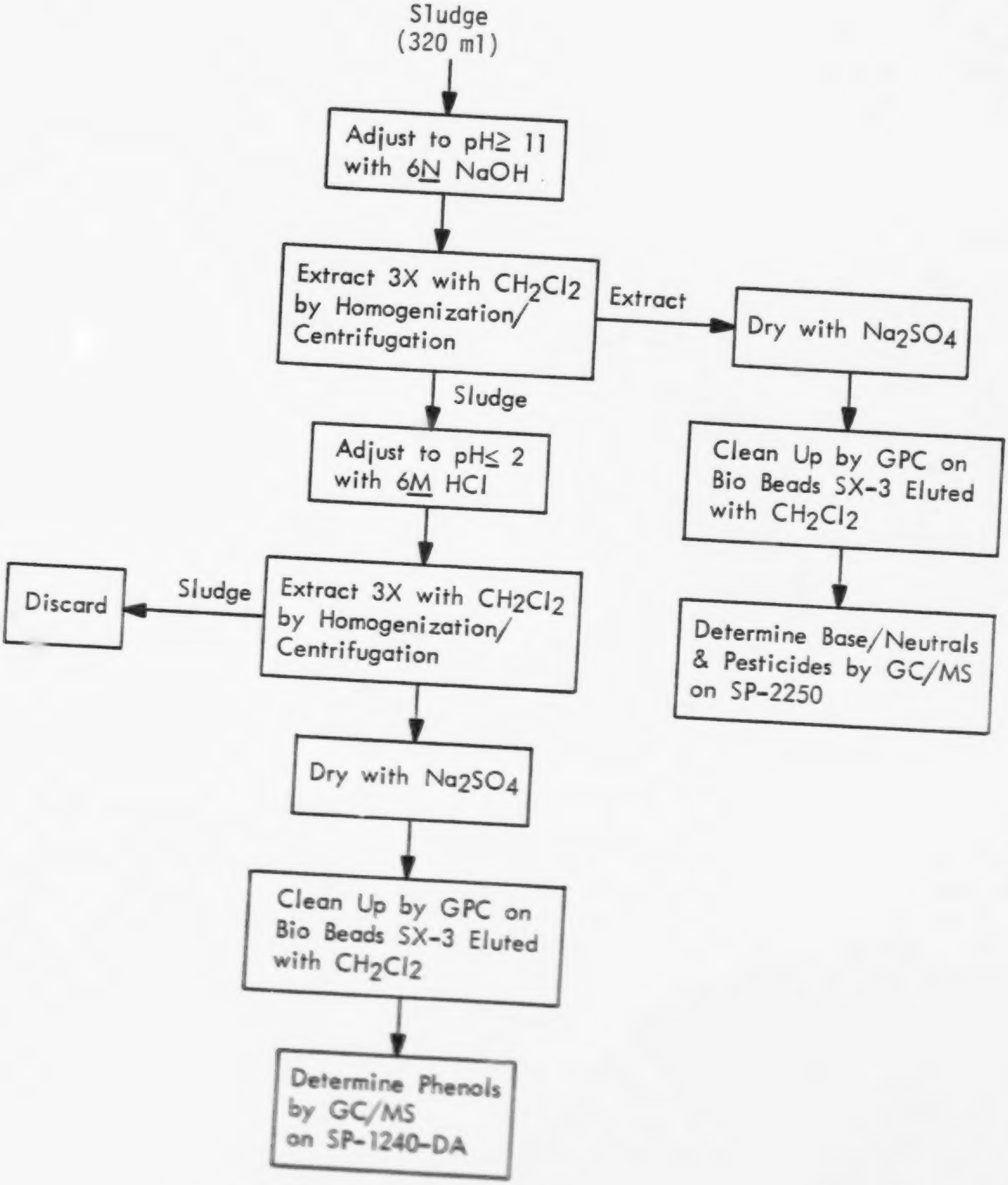
Sludge
(320 ml)
Adjust to pH≥ 11 with 6N NaOH
Extract 3X with CH2Cl2 by Homogenization/ Centrifugation
Extract
Dry with Na2SO4
Sludge
Adjust to pH≤ 2 with 6M HCl
Clean Up by GPC on Bio Beads SX-3 Eluted with CH2Cl2
Discard
Sludge
Extract 3X with CH2Cl2 by Homogenization/ Centrifugation
Determine Base/Neutrals & Pesticides by GC/MS on SP-2250
Dry with Na2SO4
Clean Up by GPC on Bio Beads SX-3 Eluted with CH2Cl2
Determine Phenols by GC/MS on SP-1240-DA

Figure 25. Dual pH extraction scheme for extractable compounds in POTW sludges.

Experimental--

Each 320-ml sludge sample was divided into four 80-ml aliquots in four 200-ml glass centrifuge screw-cap tubes. One sample for each sludge type was spiked by adding the extractable spiking compounds (in acetone) to each sludge aliquot so as to achieve a spike concentration of 310 µg/liter. The tubes were sealed with TFE-lined screw caps and were held at 4°C overnight, with tumbling, to allow equilibration of the spikes. Spiked and unspiked sludge aliquots were extracted with three portions of dichloromethane as follows. Each sludge aliquot was adjusted to pH 11 with 6 N sodium hydroxide. Sample pH was determined using indicating test strips. An 80-ml portion of dichloromethane was added to each centrifuge tube. The contents of the tube were homogenized with a Tekmar Tissumizer® blending probe for 1 min and then centrifuged at 3,000 rpm for 30 min. This produced three phases consisting of a fairly clear aqueous layer on top, a dark solvent extract on the bottom, and a firm mat of solids at the solvent-water interface. The lower solvent layer was removed with a 50-ml pipette and the extraction repeated twice. All extracts from the four tubes constituting a single sample were combined. These base neutral sludge extracts were dried by passage through a short column of anhydrous sodium sulfate[*] prior to concentration to 5 to 25 ml in Kuderna-Danish evaporators. The lowest practicable volumes were achieved while avoiding excessive viscosity or solidification of the extracts. The sludge aliquots were then adjusted to pH 1 with 6 N hydrochloric acid, and the extraction, extract drying, and extract concentration steps were repeated to produce the acidic sludge extracts.

The B/N and acidic extracts were cleaned by GPC on a 2.5-cm ID glass column packed with 50 g of Bio-Beads SX-3 and eluted with dichloromethane. The eluent flow was 5.0 ml/min with a column pressure of 350 to 700 millibars (5 to 10 psi). The column eluent passed through a 254-nm ultraviolet detector to provide some elution information. The column was calibrated by chromatographing 1.0-g aliquots of corn oil and 100-µg portions of bis(2-ethylhexyl)-phthalate and pentachlorophenol in 5.0 ml of dichloromethane. The first 100 ml eluted from the column was discarded, the second 150 ml was collected as the cleaned extract, and the final 100 ml for each run was also discarded. The "dump," "collect," and "wash" fractions were selected to provide ≧ 85% removal of the corn oil in the dump fraction, ≧ 85% recovery of the phthalate, and 100% recovery of the pentachlorophenol in the collect recovery fraction. The wash fraction, 100 ml of elution prior to the next injection, was employed to prevent carry-over. The sludge extracts were chromatographed in one or more 5.0 ml injections. The combined cleaned extract fractions were concentrated to 1 to 5 ml for GC/MS analysis. Extracts that were still highly colored were cleaned by a second pass through the GPC column.

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[*] Cleaned by extraction with dichloromethane, drying, and then heating to 650°C for 2 h. The cleaned material was stored at 116°C until just prior to its use.

The B/N and acidic extracts were analyzed by GC/MS according to the procedures described in the industrial wastewater protocol. The GC column used for analyses of B/N extracts, a 1.8 m x 2 mm ID glass column packed with 1% SP-2250 on 100/120 mesh Supelcoport, was programmed from 50 to 260°C at 10°C/min following a 4-min initial hold. The column used for analysis of acidic extracts, a 1.2 m x 2 mm ID glass column packed with 1% SP-1240-DA on 100/120 mesh Supelcoport, was programmed from 85 to 200°C at 10°C/min following a 4-min initial hold. The final column temperature was maintained for 10 min. Both columns were eluted with helium at 30 ml/min. The base/neutral and acidic compounds were quantitated by comparisons with standards prepared from the spiking solutions. Analyte concentrations were calculated using internal standard correction as follows:

$$\left(\frac{A}{B}\right)\left(\frac{B_{IS}}{A_{IS}}\right)\left(\frac{V_E}{V_I}\right)\left(\frac{N}{V_S}\right)\left(\frac{1}{F}\right) = \mu\text{g/liter of sludge}$$

where: A = area of peak in sample extract

B = area of peak in standard

A_{IS} = area of internal standard peak in sample extract

B_{IS} = area of internal standard peak in standard

V_I = volume of extract injected (μl)

V_E = total volume of extract (ml)

N = nanograms in standard

V_S = volume of sludge extracted (liter)

F = fraction of extract cleaned by GPC for analysis (e.g., $\frac{20\text{ ml}}{25\text{ ml}} = .80$).

Results and Discussion--

The results of recovery determinations for sludges spiked with the extractable spiking compounds and analyzed with the dual pH extraction scheme are shown in Table 20. Although the recoveries observed for most compounds were fairly good, several compounds were not recovered from the primary sludge. These compounds were hexachloroethane, benzidene, 3,3'-dichlorobenzidene, and pentachlorophenol. Part of the loss of hexachloroethane can be attributed to volatilization during extract concentration. Dilution of the primary sludge extracts to reduce the concentration of interfering coextractants also reduced the spike levels to at or near the detection limit. The zero recoveries observed for bis(2-chloroethyl)ether and N-nitrosodimethylamine reflect, in part, their characteristically poor chromatography.

Evaluation of a Single pH Extraction Scheme

Determination of the Recoveries of Selected Extractable Compounds at Various pHs--

Although the dual pH extraction scheme evaluated in the preceding section provided fairly good recoveries for the B/N and acidic compounds, the extraction procedure was time-consuming and labor-intensive. In an attempt to economize the effort and time required for sludge analyses, the feasibility of developing a single pH extraction scheme was investigated. An optimum pH for extraction of all of the B/N and acidic compounds was determined from the recoveries observed for representative compounds spiked into clean water and extracted at various pH levels. The optimum pH was then utilized in recovery determinations for the same compounds from spiked sludge.

Experimental--Separate 1.0 liter aliquots of glass-distilled water, spiked with 500 µg/liter each of phenol, 2,4-dinitrophenol, and pentachlorophenol were adjusted to pH 2, 3, 4, and 5 and extracted serially with three portions of dichloromethane (200, 100, and 100 ml). Additional distilled water aliquots were spiked with 500 µg/liter each of anthracene, benzidine, and 3,3'-dichlorobenzidine and similarly extracted at pH 2, 3, 4, and 11. The extracts were dried by passage through a short column of anhydrous sodium sulfate, concentrated to 1.0 ml in Kuderna-Danish evaporators, and analyzed by GC/FID. The chromatographic columns and conditions used were the same as described for GC/MS analysis of sludge extracts in the preceding section.

Results and discussion--The results of these recovery determinations are shown in Table 21. Recoveries for benzidine were very low at pH 2 and 3 but better at pH 4 and 11. Pentachlorophenol and 2,4-dinitrophenol recoveries were good at pH 2, 3, and 4 but were lower at pH 5. Anthracene was inexplicably recovered at only 54% at pH 4. Based on these results, the best compromise pH for extraction of the entire range of acidic and basic compounds appeared to be pH 4.

TABLE 20. RESULTS OF EVALUATION OF A DUAL pH EXTRACTION SCHEME (BASIC THEN ACIDIC) FOR THE ANALYSIS OF BASE/NEUTRALS AND ACIDS FROM POTW SLUDGES

Compound	Spike Level (µg/L)	Primary sludge[a]		Secondary sludge		Combined sludge	
		Unfortified conc. (µg/L)	Spike recovery (%)	Unfortified conc. (µg/L)	Spike recovery (%)	Unfortified conc. (µg/L)	Spike recovery (%)
1,4-Dichlorobenzene	310	ND[b]	150	ND	43	ND	78
Hexachloroethane	310	ND	0	ND	70	ND	150
Bis(2-chloroisopropylether	310	ND	110	ND	56	ND	100
Bis(2-chloroethyl)ether	310	ND	0	ND	0	ND	0
Acenaphthylene	310	ND	170	ND	75	ND	110
2,6-Dinitrotoluene	310	ND	94	ND	81	ND	110
Phenanthrene[c]	310	3,600	-	ND	-	460	-
Fluoranthene	310	ND	320	ND	59	180	140
Benzidene	310	ND	0	ND	39	ND	34
3,3'-Dichlorobenzidene	310	ND	0	ND	67	ND	130
Bis(2-ethylhexyl)phthalate	310	3,500	68	420	66	630	330
Benz[a]pyrene	310	94	270	7.7	80	74	150
N-Nitrosodimethylamine	310	ND	0	ND	0	ND	0
Phenol	310	400	180	ND	130	200	62
2,4-Dichlorophenol	310	ND	130	ND	110	ND	27
Pentachlorophenol	310	ND	0	ND	80	180	100

[a] The primary sludge extracts were analyzed at a 1:5 dilution relative to other extracts because of high levels of interfering materials.

[b] ND = not detected.

[c] Phenanthrene was not included in the spikes.

TABLE 21. RECOVERY OF SELECTED SEMIVOLATILE PRIORITY POLLUTANTS EXTRACTED AT SELECTED pHs

Compound	Spike level (μg/L)	Extraction recovery (%)				
		pH 2	pH 3	pH 4	pH 5	pH 11
Phenol	500	39	46	41	46	NA[a]
2,4-Dinitrophenol	500	95	95	112	44	NA
Pentachlorophenol	500	100	96	107	85	NA
Anthracene	500	73	89	54	NA	92
Benzidene	500	2	2	44	NA	73
3,3'-Dichlorobenzidene	500	70	87	71	NA	85

[a] NA = not analyzed.

Determination of the Recoveries of Selected Extractable Compounds from Sludge--

Experimental--Aliquots (320 ml) of primary sludge from the Platte County POTW and digested sludge from the Little Blue River POTW were prepared and spiked in the same manner as aliquots prepared for dual pH extraction, described in the preceding section. Triplicate spiked aliquots were prepared for each sample. The aliquots were buffered at pH 4 with 5 ml of a 0.1-M potassium hydrogen phthalate solution and extracted with dichloromethane by homogenization/centrifugation. The extracts were cleaned and concentrated by the procedures previously described for the dual pH extraction scheme. B/N and acidic compounds were determined in the extracts by GC/MS on both column systems.

Results and discussion--The results of recovery determinations for spiked sludge using the single pH extraction scheme are shown in Table 22. Recoveries were not calculated for bis(2-ethylhexyl)phthalate since it was present in the unspiked sludges at concentrations much higher than the spike level. The recoveries observed for most compounds are fairly good. However, the benzidines and chloroalkylethers were not recovered from any of the spiked sludge aliquots.

Overall, the dual pH extraction scheme gave somewhat better recoveries than those obtained with the single pH scheme. In particular, the phenols, benzidines, and chloroalkyl ethers were recovered better from spiked sludges extracted at basic and then acidic pH. Although the single pH procedure was considerably faster to perform, the dual pH scheme illustrated in Figure 25 was selected for the preliminary POTW sludge protocol[4] based on the results of the recovery determinations. Although the priority pollutant pesticides were not included in the evaluation experiments, they are typically well-behaved neutral compounds. As such, in the preliminary protocol, the pesticides were considered as a subset of the B/Ns.

ADDITIONAL METHODS DEVELOPMENT FOR MUNICIPAL AND INDUSTRIAL WASTEWATER TREATMENT SLUDGE

The combination of homogenization/centrifugation extraction and GPC extract cleanup described in the preliminary POTW sludge protocol provided satisfactory recoveries for the B/N and acidic compounds spiked into POTW sludge. However, the rigorous extraction procedure was time-consuming, labor-intensive, and not very selective. The large quantities of lipids and other high molecular weight biogenic compounds in many crude extracts exceeded the capacity of the GPC cleanup procedure. Although the GPC method was designed to remove ≥ 85% of up to 1 g of high molecular weight biogenic compounds, multiple GPC runs were required for many extracts. The multiple runs were done as sequential 5.0-ml injections of crude extracts or by rechromatographing the cleaned extracts. Some extracts that were cleaned twice and concentrated to 1.0 ml still could not be analyzed by GC/MS because of severe interferences. The time and cleanup problems were partially reduced for the EPA survey of POTW

TABLE 22. RESULTS OF EVALUATION OF A SINGLE pH EXTRACTION SCHEME FOR THE ANALYSIS OF BASE/NEUTRALS AND ACIDS FROM POTW SLUDGES

Compound	Spike level (µg/L)	Primary sludge		Secondary sludge		Combined sludge	
		Unfortified conc. (µg/L)	Spike recovery (%)	Unfortified conc. (µg/L)	Spike recovery (%)	Unfortified conc. (µg/L)	Spike recovery (%)
1,4-Dichlorobenzene	310	130	170 ± 44[a]	12	110 ± 16	29	140 ± 21
Hexachloroethane	310	ND[b]	70 ± 13	ND	57 ± 22	ND	41 ± 12
Bis(2-chloroisopropyl)ether	310	ND	0	ND	0	ND	0
Bis(2-chloroethyl)ether	310	ND	0	ND	0	ND	0
Acenaphthylene	310	ND	78 ± 3	ND	89 ± 17	6.3	100 ± 30
2,6-Dinitrotoluene	310	ND	54 ± 20	ND	68 ± 11	15	37 ± 14
Phenanthrene	310	19	81 ± 6	5.9	88 ± 9	15	72 ± 5
Fluoranthene	310	19	75 ± 14	7.9	67 ± 20	4.9	58 ± 20
Benzidine	310	ND	0	ND	0	ND	0
3,3'-Dichlorobenzidene	310	ND	0	ND	0	ND	0
Bis(2-ethylhexyl)phthalate	310	3,100	c	1,500	c	2,500	c
Benzo[a]pyrene	310	7.5	80 ± 25	3.7	90 ± 53	7.5	100 ± 15
N-Nitrosodimethylamine	310	ND	0	ND	0	ND	0
Phenol	310	91	88 ± 78	35	35 ± 6	240	89 ± 32
2,4-Dichlorophenol	310	ND	67 ± 40	2.0	37 ± 4	ND	70 ± 19
Pentachlorophenol	310	30	110 ± 76	21	45 ± 5	22	89 ± 35

[a] Mean ± standard deviation for three determinations.

[b] ND = not detected.

[c] Recovery calculations are not representative since levels in the unfortified sludges were much higher than the spiked levels.

emissions by extracting a single 80-ml sludge aliquot for each sample.[8] This required only one centrifuge tube per sample and produced 25% of the interfering coextractants in the crude extract. And, since the extracts from 80 ml aliquots could be concentrated further following cleanup, the method sensitivity was essentially the same. The experiments described below were designed to evaluate alternate procedures to allow more efficient and selective extraction, to evaluate alternate extract cleanup methods appropriate for the best extraction procedure, and to develop capillary GC/MS methods to aid in the determination of the extractable compounds in complex sludge extracts.

Extraction Methods

Three alternate extraction procedures were evaluated for sludges in an attempt to develop a more efficient, selective, and less time-consuming extraction method. The procedures evaluated include: continuous liquid-liquid extraction, steam distillation, and microextraction.

Continuous Liquid-Liquid Extraction--

A continuous liquid-liquid extraction (CLLE) apparatus, previously designed by MRI, has been successfully used for extracting industrial wastewaters for analyses of base/neutral and acidic organic priority pollutants. In addition to allowing unattended extraction, the continuous method allowed extraction of wastewaters containing high levels of dissolved and suspended solids without formation of emulsions. The apparatus, shown in Figure 26, was designed for use with heavier-than-water solvents, e.g., dichloromethane. This system was evaluated for the extraction of diluted sludge aliquots. The sludge aliquots were diluted so that the suspended solids contents were similar to those typical of high solids wastewaters. The effects of selected operating parameters pertinent to adapting the CLLE procedure for sludges were investigated. These parameters were the extraction time, the sludge aliquot dilution ratio, and the addition of methanol. Methanol was added to encourage desorption of compounds that associate strongly with the sludge solids. The desorbed compounds would then be more easily extracted.

Extraction time--Aliquots of unspiked combined sludge were extracted for 10 and 20 h to investigate the time required for most efficient extraction.

Experimental--The basic CLLE procedure is described as follows. The apparatus was assembled with the glass drip tip adjusted to a level near the top of the sample compartment and the stopcock closed. To prevent suspended solids from being carried into the boiling flask by the recycling solvent, a plug of precleaned glass wool was placed in the bottom of the sample chamber. Half of the dichloromethane, 200 ml, was loaded into the sample compartment, and the other half was loaded into the boiling flask. The sample, consisting of 1.0 liter of water or a sludge aliquot diluted to 1.0 liter, was added to the sample compartment and the stopcock was opened. The drip tip was lowered until the solvent level just entered the tip and was secured at that level with the two bored-through TFE unions. The extraction

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[8] Hansen, E. M. Midwest Research Institute, personal communication (1979).

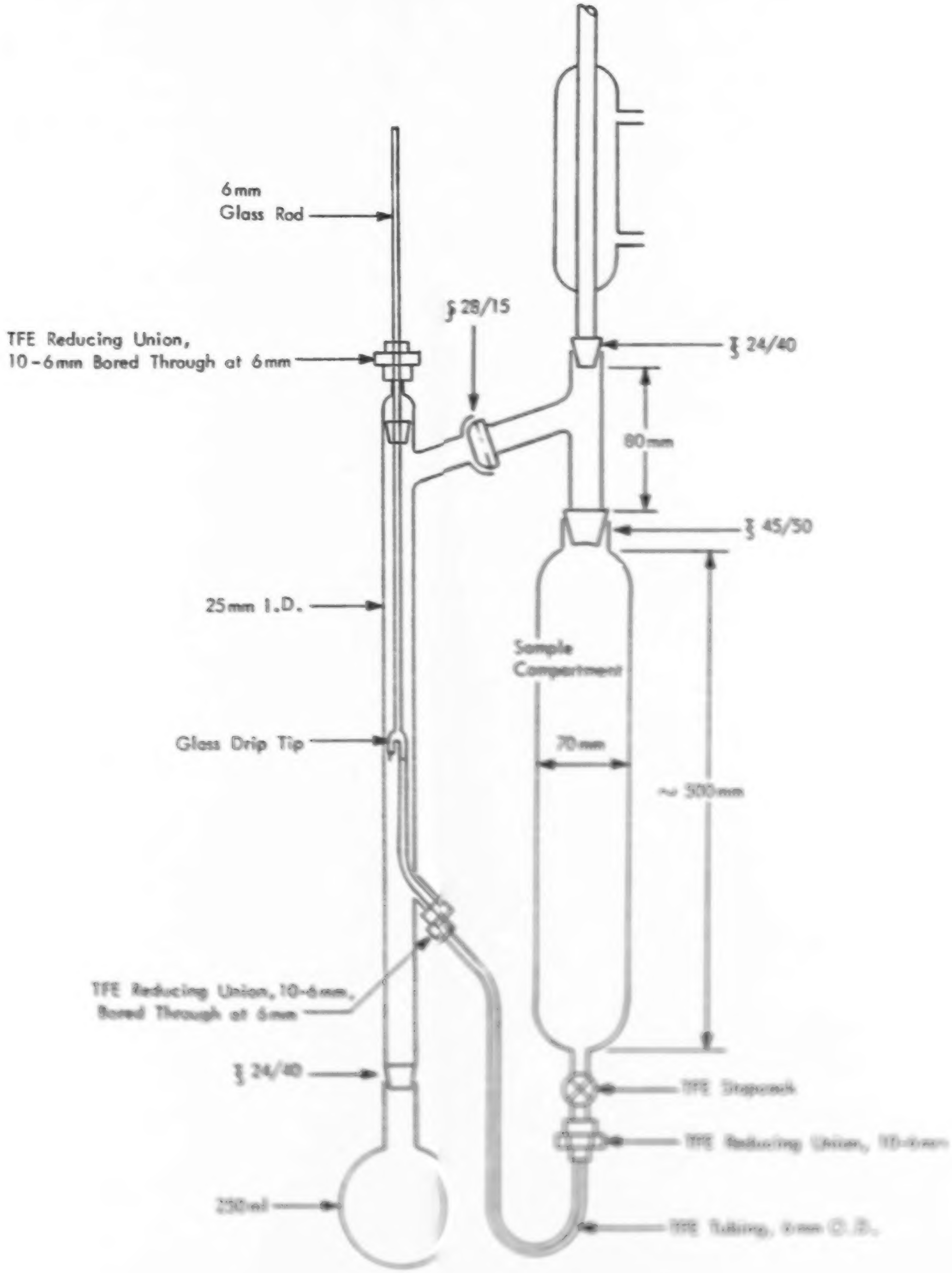
6mm
Glass Rod
TFE Reducing Union,
10-6mm Bored Through at 6mm
§ 28/15
§ 24/40
80mm
§ 45/50
25mm I.D.
Sample
Compartment
Glass Drip Tip
70mm
~ 500mm
TFE Reducing Union, 10-6mm,
Bored Through at 6mm
§ 24/40
TFE Stopcock
TFE Reducing Union, 10-6mm
250ml
TFE Tubing, 6mm O.D.

Figure 26. Continuous liquid-liquid extractor designed by MRI.

was initiated by heating the boiling flask. The vaporized solvent was condensed in the water-cooled condenser, dripped through the sample, and collected at the bottom of the sample chamber. The return tube maintained the solvent in the sample chamber at the original level. At the end of the extraction, the extracts were removed, dried by passage through a short column of precleaned anhydrous sodium sulfate, concentrated to 1.0 ml in Kuderna-Danish evaporators, and analyzed by the GC/MS procedures described in the preliminary POTW sludge protocol.

For this particular experiment, two 100-ml aliquots of unspiked combined sludge (2.1% solids) were adjusted to pH 11 with 6 N sodium hydroxide and extracted for 10 and 20 h, respectively.

Results and discussion--The results of analyses of unspiked sludge extracts prepared from 100-ml aliquots diluted to 1.0 liter and extracted at pH 11 for 10 and 20 h are shown in Table 23. The concentrations observed were essentially the same for all compounds identified except bis(2-ethylhexyl)-phthalate. The difference in phthalate concentrations is likely due to spurious contamination. From these results, it was concluded that 10 h was a sufficient extraction time.

Extract dilution--

Experimental--Two sludge aliquots, 100 and 300 ml, were spiked with the B/N spiking compounds and extracted at pH 11 as described in the preceding experiment. The extracts were analyzed by the GC/MS procedures described in the preliminary POTW sludge protocol.

Results and discussion--The influence of sludge dilution on extraction efficiencies may be seen from the spike recoveries shown in Table 24. The recoveries from the 100-ml aliquot were generally higher than from the 300-ml aliquot. During the course of extracting sludge aliquots, the suspended solids settle to the water-solvent interface. The solids tend to settle faster in the less diluted aliquot. Hence, it is likely that the sludge solids were not extracted as efficiently in that aliquot.

Addition of methanol--Aliquots of spiked water and combined sludge were extracted with and without the addition of methanol.

Experimental--Two 500-ml aliquots of glass-distilled water and two 100-ml aliquots of combined sludge were spiked with the extractable spiking compounds and were allowed to equilibrate at 4°C for 4 h. One spiked water aliquot and one spiked sludge aliquot were fortified with 200 ml of glass-distilled methanol. All water and sludge aliquots were diluted to 1.0 liter, adjusted to pH 11 with 6 N sodium sulfate, and extracted for 10 h. The B/N extracts were removed and the systems were charged with 400 ml of fresh solvent. The samples were then adjusted to pH 1 with 6 N hydrochloric acid and extracted an additional 10 h. The resulting B/N and acidic extracts were dried and analyzed by the preliminary POTW protocol GC/MS procedures.

TABLE 23. CONCENTRATIONS MEASURED IN UNSPIKED COMBINED SLUDGE EXTRACTS BY CONTINUOUS LIQUID-LIQUID EXTRACTION: EFFECT OF EXTRACTION TIME

	Concentration (μg/L sludge)	
Compound	20-h extraction	10-h extraction
1,4-Dichlorobenzene	12	11
Acenaphthylene	46	39
Fluoranthene	12	15
Pyrene	13	19
Bis(2-ethylhexyl)phthalate	650	2,000
Benzofluoranthenes[a]	6	7
Benzo[_a_]pyrene	6	5

[a] Concentrations represent sums for these compounds, which elute simultaneously and have the same major ions for GC/MS.

TABLE 24. RECOVERIES OF EXTRACTABLE COMPOUNDS FROM SPIKED COMBINED SLUDGE BY CONTINUOUS LIQUID-LIQUID EXTRACTION: EFFECT OF SLUDGE DILUTION

Compound	Spike level (μg/L sludge)	Recovery (%)	
		100-ml aliquot[a]	300-ml aliquot[a]
1,4-Dichlorobenzene	315	33	57
Hexachloroethane	317	98	46
Acenaphthylene	318	88	35
2,6-Dinitrotoluene	319	121	81
Fluoranthene	274	33	25
Benzidene	310	37	69
3,3'-Dichlorobenzidine	364	68	43
n-Butylbenzylphthalate	358	20	25
Bis(2-ethylhexyl)phthalate	336	57	6
Benzo[*a*]pyrene	312	20	26

[a] Diluted to 1.0 L prior to extraction.

Results and discussion--The results of recovery determinations for spiked water and sludge aliquots extracted with and without the addition of methanol are shown in Table 25. The recoveries observed from the spiked sludge were generally lower than from the spiked water. The addition of methanol had little influence on recoveries from water or sludge. Several compounds, e.g., polynuclear aromatic compounds, were very poorly recovered from spiked sludge. These compounds are likely to strongly associate with suspended solids. Some form of mechanical agitation during extraction may improve solids-solvent contact and increase extraction efficiencies for these compounds.

Extractive Steam Distillation--

Extractive steam distillation has been shown to be an efficient and selective procedure for concentrating chlorinated pesticides from water, soil, sediment, and tissue samples. Veith and Kiwus[9] developed an apparatus which provided extraction of the steam distillate with a lighter-than-water solvent. A distillation/extraction head is marketed by Kontes (Catalog No. K-523010) which allows continuous extraction of the distillate with a heavier-than-water solvent. This continuous extractive steam distillation system was evaluated for the extraction of sludge distillate with dichloromethane. The apparatus utilized, fashioned after the Kontes unit, is shown in Figure 27. The sample is boiled and the condensed distillate is extracted in a manner similar to the CLLE unit described previously. This system was initially evaluated with spiked water with extraction times from 2 to 72 h. The optimum extraction time as determined from these experiments was used in extraction studies with spiked combined sludge.

Extraction time--The optimum time for efficient extractive steam distillation was investigated by extracting aliquots of spiked water for 2 to 72 h.

Experimental--Aliquots of glass-distilled water (500 ml) were spiked with selected neutral or acidic compounds. Aliquots spiked with neutral compounds were adjusted to pH 7 and transferred to the sample flask. The solvent flask was charged with 300 ml dichloromethane and the contents of both flasks were heated to boiling. Individual neutral aliquots were extracted for 2, 6, 15, or 72 h. Aliquots spiked with acidic compounds, adjusted to pH 1, and similarly extracted for 2, 6, 12, or 48 h. All extracts were dried with anhydrous sodium sulfate columns, concentrated to 1.0 ml, and analyzed by GC/FID using the gas chromatographic procedures described in the preliminary POTW sludge protocol.

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[9] Veith, G. D. and L. M. Kiwus. An Exhaustive Steam Distillation and Solvent Extraction Unit for Pesticides and Industrial Chemicals. Bull. Environ. Contam. Toxicol. 17:631-36 (1977).

TABLE 25. RECOVERIES OF EXTRACTABLE COMPOUNDS FROM SPIKED DISTILLED WATER AND SPIKED COMBINED SLUDGE BY CONTINUOUS LIQUID-LIQUID EXTRACTION: EFFECT OF METHANOL (MeOH) ADDITION

	Distilled water				Combined sludge			
	Without MeOH		With MeOH		Without MeOH		With MeOH	
Compound	Spike level (µg/L)	Spike recovery (%)	Spike level (µg/L)	Spike recovery (%)	Spike level (µg/L sludge)	Spike recovery (%)	Spike level (µg/L sludge)	Spike recovery (%)
1,4-Dichlorobenzene	315	113	315	119	312	32	315	38
Hexachloroethane	317	85	317	100	314	6	317	5
Bis(2-chloroisopropyl)-ether	318	110	318	113	364	69	364	87
Bis(2-chloroethyl)ether	319	259	319	248	316	115	338	145
Acenaphthylene	318	69	318	73	315	3	318	11
2,6-Dinitrotoluene	319	120	319	118	316	51	319	60
Fluoranthene	274	73	274	77	271	8	274	8
Benzidine	310	60	310	60	316	10	316	52
3,3'-Dichlorobenzidine	364	101	364	116	371	35	371	44
n-Butylbenzylphthalate	358	34	358	25	354	14	358	14
Bis(2-ethylhexyl)-phthalate	336	44	336	52	333	a	336	a
Benzo[*a*]pyrene	312	67	312	112	309	8	312	5
Phenol	335	99	341	69	344	102	341	94
2,4-Dimethylphenol	351	4	341	13	355	19	359	27
2,4-Dichlorophenol	296	57	292	75	335	62	338	57
Pentachlorophenol	334	0	337	220	344	0	347	14

[a] Recovery not determined since the spike level was much lower than present in the unspiked sample.

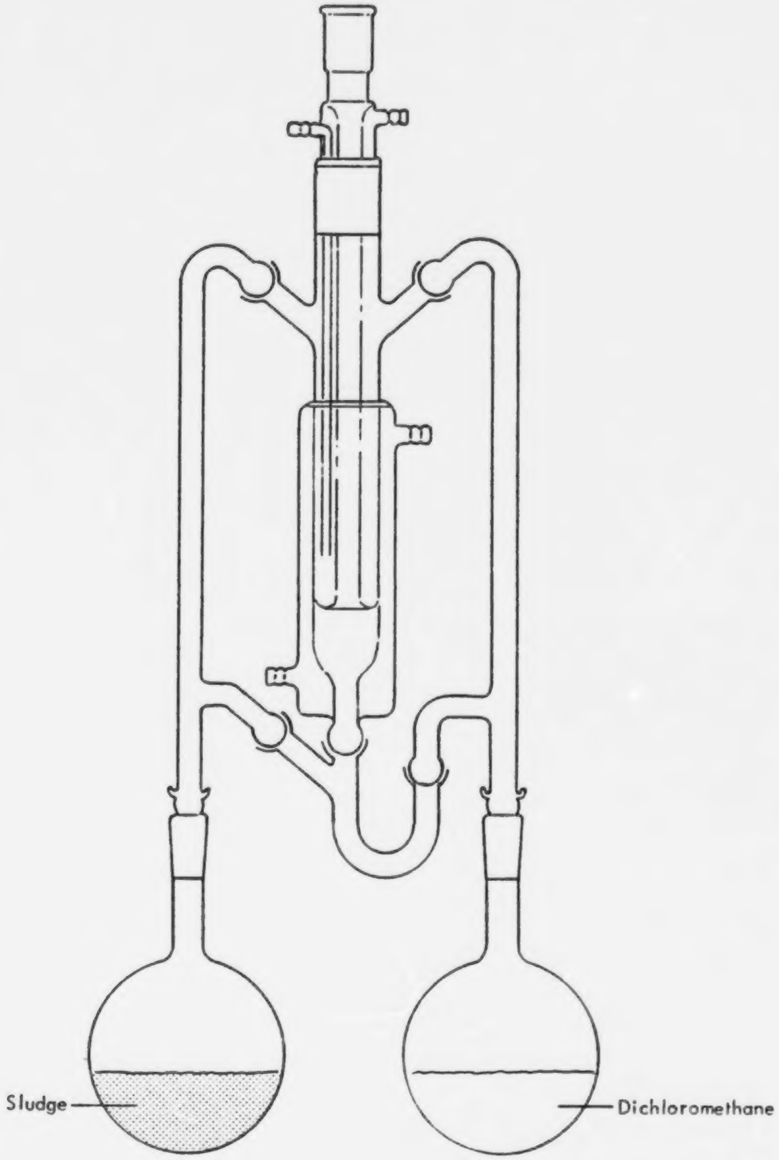
Sludge
Dichloromethane

Figure 27. Continuous extractive steam distillation apparatus.

Results and discussion--The results of the extraction time study are shown in Table 26. Maximum recoveries were achieved for most compounds except phenol after only 2 h of extraction. However, since the phenol recovery was higher for 6-h extractions, subsequent steam distillation experiments were conducted using 6 h of extraction. The low recoveries observed for 1,4-dichlorobenzene (21 to 27%) were likely due to volatility losses. Higher recoveries were observed in subsequent experiments when the condenser cooling water was chilled.

Determination of recoveries from spiked water and sludge--

Experimental--A 500-ml aliquot of glass-distilled water, spiked with the extractable spiking compounds, and a similar aliquot of unspiked water were basified to pH 11 and extracted for 6 h with 300 ml of dichloromethane. The extracts were removed and the water was acidified to pH 1 before extracting with fresh solvent. Two 300-ml aliquots of combined sludge, one spiked and one unspiked, were similarly extracted. All water and sludge extracts were dried, concentrated, and analyzed by GC/MS according to the preliminary POTW protocol.

Results and discussion--The results of recovery determinations for spiked compounds in water and sludge extracted by steam distillation are shown in Table 27. Recoveries observed for the benzidenes, butylbenzylphthalate, and 2,4-dimethylphenol were low from both water and sludge. The poor recoveries for 2,4-dimethylphenol were surprising in light of the 54 to 67% recoveries observed in the preceding experiment. This particular compound was frequently and inexplicably observed to have poor recoveries throughout the course of this program. The high recoveries observed for the chloroalkyl ethers was likely due to the difficulties inherent in measuring the response of the broad chromatographic peaks characteristic of the compounds. Nonetheless, the spike recoveries from combined sludge were considerably lower than from water for many compounds.

The probability that a particular compound can be efficiently steam distilled from aqueous media is directly related to its vapor pressure at the boiling point of the sample. Vapor pressure data are presented for selected priority pollutants and other compounds in Table 28. These data were estimated with the Antoine equation or taken from literature sources. The Antoine equation is:

$$\log_{10} P = A - B/(C + T)$$

or

$$\log_{10} P = \frac{-52.23B}{(T + 273)} + C$$

TABLE 26. RECOVERIES OF EXTRACTABLE COMPOUNDS FROM SPIKED DISTILLED WATER SAMPLES BY EXTRACTIVE STEAM DISTILLATION

Compound	Spike level (μg/L)	% Recovery					
		Time (h)					
		2	6	12	15	48	72
1,4-Dichlorobenzene	100	27	25	NA[a]	21	NA	22
Bis(2-chloroethyl)ether	100	36	35	NA	35	NA	32
2,6-Dinitrotoluene	100	100	99	NA	95	NA	74
Fluoranthene	100	81	88	NA	75	NA	72
Bis(2-ethylhexyl)phthalate	100	81	94	NA	80	NA	101
Phenol	100	42	71	73	NA	69	NA
2,4-Dimethylphenol	100	56	54	62	NA	67	NA
2,4-Dichlorophenol	100	76	61	131	NA	46	NA
Pentachlorophenol	100	99	106	125	NA	95	NA

[a] NA = Not analyzed.

TABLE 27. RECOVERIES OF EXTRACTABLE COMPOUNDS FROM SPIKED DISTILLED WATER AND SPIKED SLUDGE SAMPLES BY EXTRACTIVE STEAM DISTILLATION

Compound	Distilled water		Combined sludge	
	Spike level (μg/L water)	Spike recovery (%)	Spike level (μg/L sludge)	Spike recovery (%)
1,4-Dichlorobenzene	315	102	630	103
Hexachloroethane	317	106	634	0
Bis(2-chloroisopropyl)ether	386	143	772	154
Bis(2-chloroethyl)ether	362	176	492	258
Acenaphthylene	318	96	636	97
2,6-Dinitrotoluene	319	129	638	0
Fluoranthene	274	102	548	43
Benzidine	310	0	620	0
3,3'-Dichlorobenzidine	364	0	728	0
_n_-Butylbenzylphthalate	358	0	716	4
Bis(2-ethylhexyl)phthalate	336	71	672	17
Benzo[_a_]pyrene	316	75	624	3
Phenol	338	33	676	a
2,4-Dimethylphenol	348	3	696	0
2,4-Dichlorophenol	328	47	606	16
Pentachlorophenol	337	74	662	79

a Recovery not estimated since the concentration of phenol in the unspiked sludge was larger than the concentration in the spiked sludge.

TABLE 28. VAPOR PRESSURE DATA FOR EPA PRIORITY POLLUTANTS AND SELECTED ALIPHATIC HYDROCARBONS

Compound	P_{vap} (mm Hg)	Literature Ref.
Extractable Spiking Compounds		
1,4-Dichlorobenzene	77.7 (100°C)	a
	67 (100°C)	b
Hexachloroethane	40 (102.3°C)	c
Bis(2-chloroethyl)ether	60 (101.5°C)	c
Acenaphthylene	10^{-3}-10^{-2} (20°C)	d
Fluoranthene	10^{-6}-10^{-4} (20°C)	d
Bis(2-ethylhexyl)phthalate	0.07 (150°C)	e
Benzo[a]pyrene	5×10^{-9} (25°C)	d
Phenol	41.3 (100°C)	a
2,4-Dimethylphenol	10 (91.3°C)	c
	20 (105°C)	c
2,4-Dichlorophenol	10 (93°C)	c
	20 (108°C)	c
Pentachlorophenol	0.26 (100°C)	a
Other EPA Priority Pollutants		
1,3-Dichlorobenzene	60 (92°C)	c
1,2-Dichlorobenzene	60 (99.5°C)	c
1,2,4-Trichlorobenzene	20 (97.2°C)	c
Naphthalene	20 (101.7°C)	c
Nitrobenzene	20 (99.3°C)	c
2-Chloronaphthalene	5 (104.8°C)	c
Isophorone	20 (96.8°C)	c
Fluorene	5 (129.3°C)	c
Hexachlorobenzene	1 (114.4°C)	c
Phenanthrene	1 (118.2°C)	c
Anthracene	0.07 (100°C)	a
Dimethylphthalate	1 (100.3°C)	c
2-Nitrophenol	10 (90.4°C)	c
2-Chlorophenol	60 (92°C)	c
2,4,6-Trichlorophenol	5 (105.9°C)	c
Hydrocarbons		
n-Heptane	796 (100°C)	a
n-Octane	351 (100°C)	a
n-Nonane	158 (100°C)	a
n-Decane	72 (100°C)	a
n-Pentadecane	1.6 (100°C)	a

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a Lange's Handbook of Chemistry, 11th edition. McGraw-Hill, 1973.

b Kirk-Othmer Encyclopedia of Chemical Technology, 2nd edition. John Wiley and Sons, 1964.

c Chemical Engineer's Handbook, 5th edition. Perry and Chilton, Eds. McGraw-Hill, 1973.

d U.S. Environmental Protection Agency. Water-Related Environmental Fate of 129 priority Pollutants, Vol. II. EPA-440/4-79-029a,b, December 1979.

e Kirk-Othmer Encyclopedia of Chemical Technology, 1st edition. John Wiley and Sons, 1953.

where A , B , and C are constants characteristic of the compound and T is the temperature in degrees Celsius. From these data, it is not surprising that extractive steam distillation recoveries for benzo[a]pyrene are low. Vapor pressure data were not available for the benzidenes; however, benzidene boils at 400°C, so the vapor pressures for benzidene and 3,3'-dichlorobenzidine are likely to be very low at 100°C and their potentials to steam distill are thus not favorable.

Although the concentrated steam distillation extracts from the combined sludge were very clear and were analyzed without cleanup, they contained high levels of aliphatic hydrocarbons. This is not surprising considering that the vapor pressures for the alkanes listed in Table 28 are high relative to the extractable priority pollutants.

Microextraction--

Successful liquid-liquid extraction of aqueous samples with a small volume of solvent was reported by Rhoades and Millar.[10] This method has been adapted to allow simple and rapid extraction of organic priority pollutants from a variety of industrial wastewaters.[11] This procedure typically involves shaking 100 ml of wastewater with 1.0 ml of hexane, diisopropyl ether, toluene, or other lighter-than-water solvent, as appropriate for the specific analytes, in a 100-ml volumetric flask. Following extraction the contents of the flask are allowed to settle. The solvent accumulates in the constricted neck and can be sampled with a syringe for a direct GC or GC/MS analysis. Salt is added and/or the pH of the sample can be adjusted as required to optimize recoveries. Although the procedure was designed for use with lighter-than-water solvents, glassware can be envisioned that could allow extraction with heavier-than-water solvents, such as dichloromethane. However, the suspended solids in sludge and diluted sludge would likely hinder the recovery of the extract from the bottom of the sample. In addition to its simplicity, microextraction typically produces extracts that are relatively free of interfering coextracted materials. The solvent to sample ratio (typically 1:100) efficiently extracts only those compounds with favorable partitioning characteristics. The interferences in many samples that are extracted by more rigorous procedures frequently have low partitioning coefficients but are present in the samples in very high concentrations.

Microextraction procedures were evaluated for sludges with a few minor modifications. Specifically, sludge samples were extracted in Babcock milk butterfat testing tubes. Babcock tubes, shaped much like volumetric flasks but designed to tolerate centrifugation, were used to assist extract recovery from the extracted sludge aliquots. Following a preliminary experiment in which spiked combined sludge was extracted with hexane, the influences of salting and solvent selection were investigated with spiked water and combined sludge.

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[10] Rhoades, J. W. and J. D. Millar. Gas Chromatographic Method for Comparative Analysis of Fruit Flavors. J. Agr. Food Chem. 13:5-9 (1965).

[11] Rhodes, J. W. and C. P. Nulton. Southwest Rsearch Institute, personal communication (1979).

Preliminary evaluations with spiked combined sludge--

Experimental--Two 15-ml aliquots of combined sludge (2.1% solids) were transferred to Babcock tubes and spiked with selected B/N compounds. All aliquots were diluted to 45 ml with glass-distilled water. After adjusting to pH 11, a 0.5-ml aliquot of hexane was added to each tube, and the tubes were hand-shaken for 2 min. In order to recover the extracts, the tubes were centrifuged for 15 min at 1,500 rpm. The extracts were analyzed directly by GC/FID using the SP-2250 packed column system described in the preliminary POTW sludge protocol.

Results and discussion--The recoveries determined for spiked compounds concentrated from combined sludge by microextraction are shown in Table 29. Since the maximum enrichment achievable for the preliminary evaluations was 30-fold (0.5 ml extract from 15-ml sludge aliquot), high spike levels were employed. Although the spike levels were rather high and some differences were apparent between the recoveries observed for duplicates, these results indicated that the microextraction procedure showed some promise. Appropriate choices of extracting solvent may facilitate analysis of the entire range of extractable compounds. The possible necessity of using several extraction solvents on replicate sludge aliquots may still be preferable to a laborious and difficult extraction and extract cleanup scheme. The extracts appeared to be relatively free from coextracted interferences. This was evidenced by the successful determination of spiked compounds by GC/FID. The GC/FID chromatograms for the microextracts of spiked and unspiked sludge shown in Figure 28 illustrate that the spiked compounds were readily identified.

Recoveries from spiked water--Three solvents were evaluated and the influence of salting was investigated for microextraction of spiked water.

Experimental--Several aliquots (100 ml) of glass-distilled water were extracted in 100-ml volumetric flasks. Separate aliquots were spiked with the B/N and acidic spiking compounds and were adjusted to pH 11 or 1, as appropriate. The water samples were extracted with 1.0-ml aliquots of hexane, toluene, or diisopropylether. The extracts were removed with pipettes and the process was repeated twice for a total of three extractions for the same spiked water aliquot. An additional set of extractions was conducted in a similar fashion for glass-distilled water saturated with sodium chloride. All individual extracts were analyzed without concentration by GC/FID using the chromatographic systems described in the preliminary POTW sludge protocol. The contents of the extracts were quantitated against mixed standard solutions prepared in the same solvent.

Results and discussion--The results of microextraction recovery determinations with the three solvents and with or without salt are shown in Tables 30 to 32. In general, toluene provided the best recoveries for most compounds. Good recoveries were obtained with toluene for all compounds except phenol. Although good recoveries were achieved with hexane for several neutral compounds, recoveries were generally poor for the polar compounds and for benzo[a]pyrene. Some of the polar compounds, notably bis(2-chloroethyl)-ether, 3,3'-dichlorobenzidene, and the phenols, were extracted with diisopropyl ether. Phenol has relatively high solubility in water, as noted in Section 7.

TABLE 29. MICROEXTRACTION OF EXTRACTABLE COMPOUNDS FROM SPIKED SLUDGE SAMPLES WITH HEXANE

Compound	Spike level (μg/L sludge)	Spike recovery[a] (%)
1,4-Dichlorobenzene	5,250	53, 43
Hexachloroethane	5,280	52, 26
Acenaphthylene	5,300	101, 85
2,6-Dinitrotoluene	5,320	31, 35
Fluoranthene	4,570	77, 47
_n_-Butylbenzylphthalate	5,970	85, 54
Bis(2-ethylhexyl)phthalate	5,600	52, 74
Benzo[_a_]pyrene	2,000	8, 44

[a] Sludge samples were spiked after dilution 1:1 with distilled water.

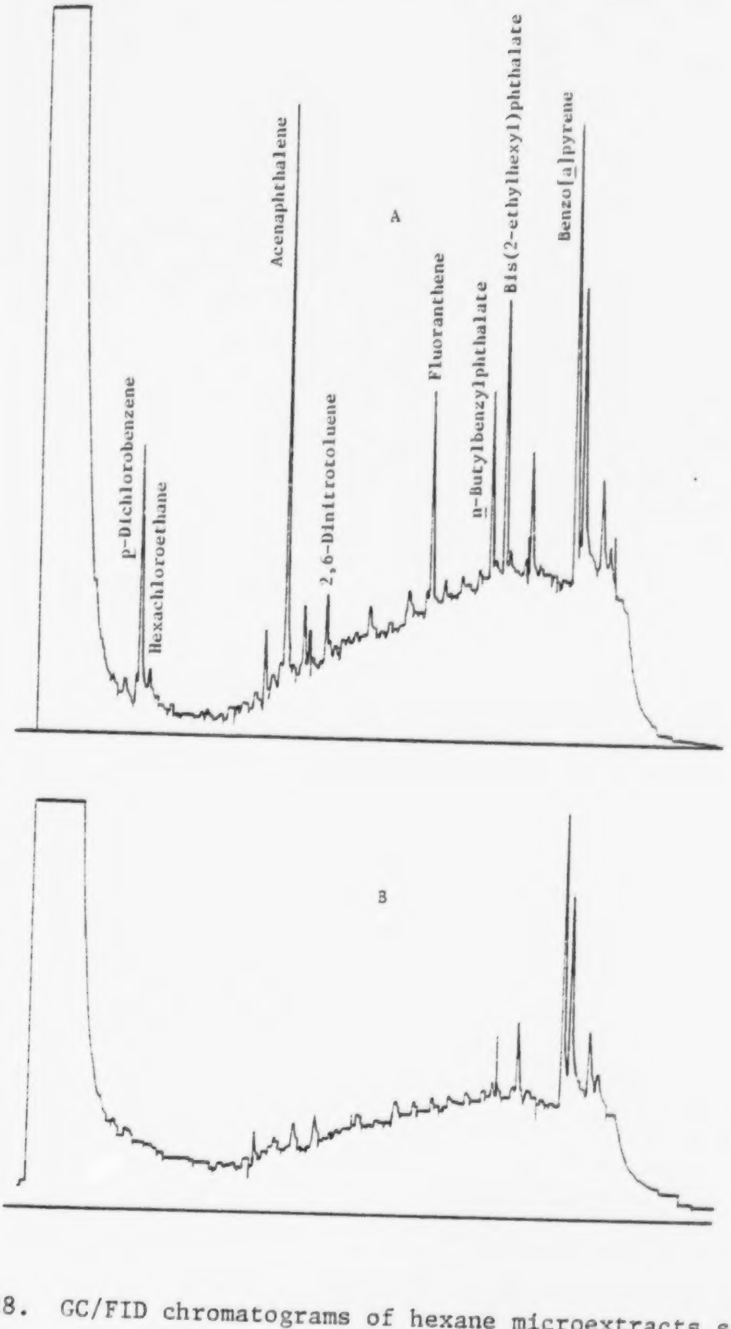


Figure 28. GC/FID chromatograms of hexane microextracts spiked (A) and unspiked (B) combined sludge.

TABLE 30. MICROEXTRACTION OF PRIORITY POLLUTANTS FROM SPIKED WATER SAMPLES WITH HEXANE

Compound	Spike level (µg/L)	Spike recovery (%)							
		With salt				Without salt			
		Extract				Extract			
		1	2	3	Sum	1	2	3	Sum
1,4-Dichlorobenzene	788	93	0	0	93	43	0	0	43
Hexachloroethane	792	81	0	0	81	42	0	0	42
Bis(2-chloroisopropyl)ether	324	0	0	0	0	0	0	0	0
Bis(2-chloroethyl)ether	211	45	16	4	65	83	4	0	87
Acenaphthylene	795	77	6	0	83	50	0	0	50
2,6-Dinitrotoluene	798	19	13	0	32	39	0	0	39
Fluoranthene	686	80	12	9	101	50	0	0	50
Benzidine	287	0	0	0	0	0	0	0	0
3,3'-Dichlorobenzidine	272	28	14	17	59	75	6	3	84
n-Butylbenzylphthalate	896	53	5	0	58	60	0	0	60
Bis(2-ethylhexyl)phthalate	840	62	19	6	87	50	0	0	50
Benzo[*a*]pyrene	300	26	19	0	45	53	0	0	53
Phenol	338	0	0	0	0	0	0	0	0
2,4-Dimethylphenol	348	2	2	0	4	34	15	13	62
2,4-Dichlorophenol	395	19	16	0	35	67	24	13	104
Pentachlorophenol	337	137	2	0	139	48	19	4	71

TABLE 31. MICROEXTRACTION OF PRIORITY POLLUTANTS FROM SPIKED WATER SAMPLES WITH TOLUENE

Compound	Spike level (μg/L)	Spike recovery (%)							
		With salt				Without salt			
		Extract				Extract			
		1	2	3	Sum	1	2	3	Sum
1,4-Dichlorobenzene	788	97	0	0	97	79	0	0	79
Hexachloroethane	792	73	0	0	73	73	0	0	73
Bis(2-chloroisopropyl)ether	331	0	0	0	0	102	0	0	102
Bis(2-chloroethyl)ether	209	114	13	11	138	114	0	0	114
Acenaphthylene	795	76	11	0	87	71	6	0	77
2,6-Dinitrotoluene	798	75	0	0	75	55	0	0	55
Fluoranthene	686	32	18	9	59	78	5	0	83
Benzidine	303	21	16	0	37	206	46	10	262
3,3'-Dichlorobenzidine	286	108	11	0	119	110	8	6	124
n-Butylbenzylphthalate	896	30	11	0	41	75	0	0	75
Bis(2-ethylhexyl)phthalate	840	35	17	7	59	80	7	0	87
Benzo[*a*]pyrene	300	9	0	0	9	65	0	0	65
Phenol	338	4	0	0	4	16	9	0	25
2,4-Dimethylphenol	348	35	18	11	64	87	27	11	125
2,4-Dichlorophenol	395	51	22	10	83	64	23	10	97
Pentachlorophenol	337	121	22	0	143	97	21	0	118

TABLE 32. MICROEXTRACTION OF PRIORITY POLLUTANTS FROM SPIKED WATER SAMPLES WITH DIISOPROPYL ETHER

		Spike recovery (%)							
	Spike	With salt				Without salt			
	level	Extract				Extract			
Compound	(μg/L)	1	2	3	Sum	1	2	3	Sum
1,4-Dichlorobenzene	788	45	0	0	45	34	0	0	34
Hexachloroethane	792	54	0	0	54	30	0	0	30
Bis(2-chloroisopropyl)ether	334	0	0	0	0	0	0	0	0
Bis(2-chloroethyl)ether	211	54	12	19	85	90	0	0	90
Acenaphthylene	795	67	9	0	76	58	10	0	68
2,6-Dinitrotoluene	798	32	0	0	32	55	0	0	55
Fluoranthene	686	41	13	0	54	54	12	0	66
Benzidine	303	0	0	0	0	45	14	9	68
3,3'-Dichlorobenzidine	286	77	7	0	84	99	6	0	105
_n_-Butylbenzylphthalate	896	0	0	0	0	70	43	0	113
Bis(2-ethylhexyl)phthalate	840	0	25	0	25	62	31	0	93
Benzo[_a_]pyrene	300	0	0	0	0	49	0	0	49
Phenol	338	24	19	16	59	34	37	17	88
2,4-Dimethylphenol	348	84	39	14	137	57	38	9	104
2,4-Dichlorophenol	395	140	43	9	192	58	45	11	114
Pentachlorophenol	337	68	35	20	123	61	42	31	134

Since the success of microextraction depends on a very favorable partition coefficient, high recoveries for phenol may be difficult to achieve with this technique.

The influence of the addition of salt to the aliquots prior to extraction varied with the compound spiked. In particular, recoveries for 1,4-dichlorobenzene were markedly higher when salt was added. Recoveries for benzo[a]pyrene were higher from aliquots without salt. Salting decreased recoveries for 3,3'-dichlorobenzidine extracted with hexane but did not significantly affect its extraction with toluene or diisopropylether. Hence, a successful microextraction method for sludges may necessitate extraction of replicate aliquots at different pHs, with different solvents, and with or without the addition of salt.

The largest fractions of analyte recovered by compound-solvent-salt combinations for which good total recoveries were achieved, were contained in the first of the three successive extracts. Since the success of microectraction procedures depends on very favorable partitioning characteristics, this is an important element in the potential for successful sludge microextraction. Attempts to improve recoveries by compositing successive extracts increases the likelihood of coextracting interfering materials with lower partition constants. Similarly, compositing extracts from more than one solvent-salt combination in order to analyze a wide range of compounds with a minimum of GC/MS runs would increase the potential for interferences.

Recoveries from spiked sludge--The evaluations of three solvents and salting for microextraction were repeated for spiked combined sludge (2.1% solids). Two sludge spiking levels were employed.

Experimental--Spiked and unspiked 30-ml aliquots of combined sludge were poured into Babcock tubes. Separate aliquots were spiked with the B/N and acidic compounds nominally at 200 and 1,000 µg/liter. All sludge aliquots spiked at 1,000 µg/liter were allowed to equilibrate at 4°C overnight with tumbling. The aliquots were adjusted to pH 11 or 1, as appropriate, and were diluted with 15 ml of glass-distilled water that had been saturated with the extracting solvent. The diluted aliquots were extracted with 0.5-ml aliquots hexane or toluene or 1.0 ml of diisopropylether by hand shaking for 2 min. The extracts were recovered by centrifuging at 1,500 rpm for 15 min and removing the solvent with a 500-µl syringe. The volumes of extracts recovered were read from the syringe. All extractions were conducted in duplicate. The extracts were analyzed by the GC/MS procedures described in the preliminary POTW sludge protocol.

Results and discussion--The results of microextraction recovery determinations from spiked sludge are shown in Tables 33 to 35. Few analyte recoveries were acceptable for an analytical method. The primary breakdown of the method was extract recovery. Extract recoveries were both variable and low. Essentially, no extract could be recovered from many of the acidified sludge aliquots.

TABLE 33. MICROEXTRACTION OF EXTRACTABLE COMPOUNDS FROM SPIKED SLUDGE SAMPLES WITH HEXANE

Compound	Spike level (μg/L sludge)	Spike recovery (%)				Spike[b] level (μg/L sludge)	Spike recovery (%)			
		With NaCl		Without NaCl			With NaCl		Without NaCl	
		V[a] = 330 μl	V = 400 μl	V = 230 μl	V = 220 μl		V = 870 μl	V = 1,630 μl	V = 1,220 μl	V = 1,200 μl
1,4-Dichlorobenzene	312	8	4	71	92	1,570	36	34	51	51
Hexachloroethane	208	0	0	41	45	1,040	0	0	0	0
Bis(2-chloroiso-propyl)ether	c	c	c	c	c	1,655	63	70	48	53
Bis(2-chloro-ethyl)ether	c	c	c	c	c	1,055	22	26	10	11
Acenaphthalene	190	6	5	40	45	950	26	22	51	53
2,6-Dinitrotoluene	234	3	3	0	0	1,170	0	0	0	0
Fluoranthene	180	7	4	15	15	900	5	0	31	38
Benzidine	207	0	0	c	c	1,020	0	0	0	0
3,3'-Dichloro-benzidine	243	0	0	c	c	1,200	0	4	10	14
n-Butylbenzyl-phthalate	301	10	6	23	20	1,510	9	0	84	88
Bis(2-ethylhexyl) phthalate	264	58	44	149	167	1,320	11	0	23	24
Benzo[a]pyrene	200	3	4	10	11	1,000	0.4	0.2	9	12
		V = 100 μl	V = 50 μl	V = 0 μl	V = 0 μl		V = 100 μl	V = 140 μl	V = < 10 μl	V = 10 μl
Phenol	225	0	0	-	-		0.4	0.3	0	0
2,4-Dimethylphenol	225	2.5	3	-	-		0.3	0.3	0	0.01
2,4-Dichlorophenol	219	0	0	-	-		1	1	0	0.06
Pentachlorophenol	232	6	0	-	-		0	0	0	0.07

[a] V = volume of extract recovered.

[b] Given as the average value for the four samples.

[c] Not present in the spiking solution.

TABLE 34. MICROEXTRACTION OF EXTRACTABLE COMPOUNDS FROM SPIKED SLUDGE SAMPLES WITH TOLUENE

Compound	Spike level (µg/L sludge)	Spike recovery (%)				Spike[b] level (µg/L sludge)	Spike recovery (%)			
		With NaCl		Without NaCl			With NaCl		Without NaCl	
		V[a] = 100 µl	V = 690 µl	V = 380 µl	V = 320 µl		V = 1,380 µl	V = 615 µl	V = 830 µl	V = 45 µl
1,4-Dichlorobenzene	312	0	0	10	9	1,570	0	9	14	3
Hexachloroethane	208	0	0	0	0	1,040	0	0	0	0
Bis(2-chloroisopropyl)ether	c	c	c	c	c	1,650	0	25	0	4
Bis(2-chloroethyl)ethe	c	c	c	c	c	1,055	0	0	0	5
Acenaphthylene	190	19	20	11	10	950	0	7	35	4
2,6-Dinitrotoluene	234	0	0	0	0	1,170	0	0	0	0
Fluoranthene	180	34	32	13	6	900	0	0.3	0	0.5
Benzidine	207	0	0	0	0	1,030	0	0	0	0
3,3'-Dichlorobenzidine	243	0	0	9	7	1,210	0	4	20	1.5
n-Butylbenzylphthalate	301	29	21	8	9	1,510	0	0	0	0.5
Bis(2-ethylhexyl) phthalate	264	224	200	73	80	1,320	10	0	c	c
Benzo[a]pyrene	200	0	0	9	5	1,000	0	0	0	-/2
		V = 0 µl	V = 0 µl	V = 0 µl	V = 0 µl		V = 10 µl	V = 70 µl	V = 0 µl	V = 0 µl
Phenol	225[d]	-	-	-	-	1,130	NA	e	-	-
2,4-Dimethylphenol	225[d]	-	-	-	-	1,160	NA	1	-	-
2,4-Dichlorophenol	219[d]	-	-	-	-	990	NA	1	-	-
Pentachlorophenol	232[d]	-	-	-	-	1,120	NA	0	-	-

[a] V = volume of extract recovered.

[b] Given as the average value for the four samples.

[c] Not present in the spiking solution.

[d] No solvent could be recovered from the spiked sludge.

[e] Not estimated since concentration of phenol in the unspiked sludge was found to be larger than the concentration in the spiked sludge.

NA = not analyzed.

TABLE 35. MICROEXTRACTION OF EXTRACTABLE COMPOUNDS FROM SPIKED SLUDGE SAMPLES WITH DIISOPROPYL ETHER

Compound	Spike level (µg/L sludge)	Spike recovery (%)				Spike[b] level (µg/L sludge)	Spike recovery (%)			
		With NaCl		Without NaCl			With NaCl		Without NaCl	
		V[a] = 310 µl	V = 430 µl	V = 220 µl	V = 195 µl		V = 750 µl	V = 950 µl	V = 40 µl	V = 165 µl
1,4-Dichlorobenzene	312	0	0	0	0	1,570	19	19	3	9
Hexachloroethane	208	0	0	0	0	1,040	0	0	0	0
Bis(2-chloroisopropyl)ether	c	c	c	c	c	1,650	106	74	6	19
Bis(2-chloroethyl)ether	c	c	c	c	c	1,055	45	47	1	7
Acenaphthylene	190	0	0	0	0	950	12	15	3	14
2,6-Dinitrotoluene	234	0	0	0	0	1,170	0	0	0	0
Fluoranthene	180	0.6	3	0.6	1.1	900	5	5	1	7
Benzidine	207	0	0	0	0	1,030	0	0	0	0
3,3'-Dichlorobenzidine	243	0	0	0	0	1,210	33	54	8	49
n-Butylbenzylphthalate	301	0.8	3.5	0.3	0	1,510	9	10	4	17
Bis(2-ethylhexyl) phthalate	264	12	27	4	4	1,320	35	40	12	39
Benzo[a]pyrene	200	0	0	0	0	1,000	6	7	2	8
		V = 180 µl[d]	V = 880 µl[d]	V = 400 µl[d]	V = 390 µl[d]		V = 0 µl	V = 0 µl	V = 0 µl	V = 0 µl
Phenol	225	1	5	0	0	e	-	-	-	-
2,4-Dimethylphenol	225	1.4	1.3	0	0	e	-	-	-	-
2,4-Dichlorophenol	219	0.8	0	0	0	e	-	-	-	-
Pentachlorophenol	232	0	0	0	0	e	-	-	-	-

a V = volume of extract recovered.

b Given as the average value for the four samples.

c Not present in the spiking solution.

d An additional 0.5 ml of diisopropyl ether was added after concentration.

e Experiment not performed since the solvent could not be recovered from the unspiked sludge.

Method Selection--

The alternate extraction procedures evaluated, continuous liquid-liquid extraction, extractive steam distillation, and microextraction, were selected because they are less time-consuming and less labor-intensive than homogenization/centrifugation and they may produce extracts that require little or no cleanup prior to GC/MS analysis. However, none of the techniques tested provided efficient extraction of the entire range of base/neutral and acidic compounds. Each of these procedures achieved promising recoveries for concentrating spiked compounds from clean water. Recoveries from spiked combined POTW sludge, however, were generally lower. Continuous liquid-liquid extraction with dichloromethane proved ineffective in extracting polynuclear aromatic hydrocarbons and similar hydrophobic compounds from sludge solids. Extractive steam distillation with dichloromethane was ineffective in extracting compounds with low vapor pressures. In addition, the steam distillate extracts of sludge contained high levels of coextracted aliphatic hydrocarbons. Although good recoveries were obtained for spiked water with microextraction and the procedure is exceptionally simple, the physical recovery of the organic solvent extracts from sludge aliquots was a major hindrance. Hence, the homogenization/centrifugation method was selected for the revised sludge protocol. This selection necessitated additional evaluation of extract cleanup procedures alternate or supplemental to the GPC method used in the preliminary POTW protocol.

Extract Cleanup Methods

Successful employment of a rigorous, nonselective extraction procedure for sludges, such as homogenization/centrifugation, necessitates the use of very selective extract cleanup to produce extracts of efficient quality for reliable GC/MS determination. Two extract cleanup mechanisms were evaluated to meet these requirements, molecular size discrimination and polarity selection. Various GPC procedures were evaluated to determine the optimum molecular size fractionation procedure. The polarity-based cleanup methods evaluated were adsorption chromatography on silica gel, florisil, and cesium silicate. The performance of adsorption procedures were evaluated for sludge extracts both with and without GPC precleaning.

Gel Permeation Chromatography--

Extract cleanup by preparative GPC is a molecular size discrimination technique using a low pressure column. The method employed in the preliminary POTW sludge protocol used a 2.5-cm ID column packed with Bio-Beads SX-3. The column was operated at 350 to 700 millibars (5 to 10 psi) and was eluted with 5.0 ml/min dichloromethane. Compounds that are larger than the molecular exclusion limit of the bead pores are excluded from the beads and are eluted with the first few column void volumes. Compounds that are smaller than the exclusion limit are retained in the pores and are eluted later than the excluded material. Specifically, the large biogenic compounds in sludge extracts are excluded from the bead pores and are eluted earlier than the analytes retained in the pores. Since no residue remains on the column and the column is not deactivated by the sample, the column can be reused many times and is amenable to automatic operation. The GPC system utilized for this method development was an automated system capable of processing 23 injections unattended.

Five GPC packings were evaluated with three solvent systems and one packing was evaluated with a fourth solvent system. The basic properties of the gels are their molecular weight exclusion limits, i.e., pore size, and their swelling characteristics. The nominal molecular weight exclusion limits for the five gels are listed in Table 36. The effective exclusion limits are influenced somewhat by bead swelling. Swelling characteristics are largely dependent on the bead composition but are also influenced by the solvent. The solvent influence on swelling is sufficient that injection of an extract onto a GPC column eluted with a different solvent can cause a dramatic change in the pressure in the column. Hence, extracts should be prepared in the same solvent as the eluting solvent. The solvent systems evaluated were designed to investigate the effect of solvent polarity on the column elution characteristics. The solvents tested were dichloromethane, 15% cyclohexane in dichloromethane, and 50% cyclohexane in dichloromethane. In addition, a very polar solvent 50% acetone in dichloromethane was tested with Bio-Beads SX-4.

Each gel-solvent combination was evaluated by chromatographing solutions of corn oil, butylbenzylphthalate, and mixed phenols. Corn oil was used to represent the large biogenic materials in sludge extracts. Butylbenzylphthalate is one of the largest extractable priority pollutants and thus is one of the first to elute. The mixed phenols solution contained phenol, 2,4-dichlorophenol, and pentachlorophenol. These compounds form weak hydrogen bonds with beads. As a result they are some of the later eluting analytes. The objective of the elution experiments was to achieve maximum separation between the corn oil and the phthalate and to allow good recovery of the phenols. Recoveries of selected compounds were determined for the optimum GPC procedure.

Elution patterns--

Experimental--Columns were prepared from 60 to 70 g of each packing. The gel was soaked overnight in the first solvent tested. The columns (60 cm x 2.5 cm ID fitted with adjustable plungers on both ends) were prepared by pouring the gel slurry into the column, initiating the eluent flow (up-flow at 5.0 ml/min with a constant flow pump), and compressing the bed to achieve 350 to 700 millibars of solvent pressure. The column was allowed to equilibrate at least 2 h with flow. Solutions of corn oil, butylbenzylphthalate, and mixed phenols (phenol, 2,4-dichlorophenol, and pentachlorophenol) were prepared in the elution solvent. The concentration of corn oil was 400 mg/ml. The concentrations of phthalate and phenols in the solutions were 20 to 180 µg/ml. These solutions were introduced onto the column in 5.0-ml injections. Column elution was monitored with a 254-nm absorption detector. The eluent solvent was changed for the next experiment by lowering the pressure on the bed by backing off the plungers and changing the contents of the solvent reservoir. The beads were allowed to equilibrate with the new solvent by pumping for 2 to 4 h before the bed was compressed again and equilibrated under pressure for 2 h.

TABLE 36. MOLECULAR WEIGHT EXCLUSION LIMITS FOR THE GPC PACKINGS EVALUATED

Manufacturer	Packing	Molecular weight exclusion limit[a]
Bio-Rad Laboratories	Bio-Beads SX-2	2,700
Bio-Rad Laboratories	Bio-Beads SX-3	2,000
Bio-Rad Laboratories	Bio-Beads SX-4	1,400
Bio-Rad Laboratories	Bio-Beads SX-8	1,000
Pharmacia	Sephadex LH-20	5,000

[a] Obtained from manufacturer's catalog or technical representative.

Results and discussion--The elution volumes for corn oil, butylbenzylphthalate, and the phenols are shown in Table 37. Figure 29 shows the superimposed chromatograms for the three injections on each gel eluted with 15% cyclohexane in dichloromethane. Figure 30 shows a similar comparison of chromatograms for SX-3 eluted with the three solvents. The elution volumes and peak profiles observed indicate that gels with lower molecular weight exclusion limits provided better peak shapes. In particular, the phenols elute in a narrow band on the SX-4 and -8 profiles shown in Figure 29. This may be at least partially attributed to denser packing of the column. The gels with higher exclusion limits swell more and result in columns that are more compressible. In particular, columns packed with SX-2 and -3 were very elastic. The beds could be compressed several centimeters with both plungers. Columns packed with SX-8 were barely compressible.

Although the chromatograms shown in Figure 29 do not show discernible trends for resolution between the corn oil and the phthalate, elution data for all gel-solvent combinations indicate that the lower exclusion limit gels provided generally poorer separations. In addition, as illustrated in Figure 30 for SX-3, elution with higher percentages of cyclohexane in dichloromethane resulted in poorer corn oil-phthalate separation. The best overall separation was obtained with SX-3 eluted with dichloromethane, the method used in the preliminary POTW sludge protocol. This system had the best combination of separation and peak shape. A fraction cut selected at the valley between the corn oil and phthalate achieved ≧ 85% elimination of the oil from the analytes with ≧ 85% recovery of the phthalate (based on peak areas). The selection of dichloromethane as the elution solvent is directly compatible with the homogenization/centrifugation sludge extracts.

Determination of recoveries--The recoveries of the extractable spiking compounds through GPC on Bio-Bead SX-3 eluted with dichloromethane were determined by chromatographing spiked blank extracts.

Experimental--A 1.0-ml mixed standard solution containing the extractable spiking compounds at 100 µg/ml in dichloromethane was chromatographed on the Bio-Beads SX-3 column described above. The column was eluted with dichloromethane at 5.0 ml/min. The initial 110 ml (22 min) of eluent was discarded. The next 125 ml (25 min) was collected, evaporated to 1.0 ml, and analyzed by GC/FID using the chromatographic procedures in the preliminary POTW protocol. A second 1.0-ml aliquot of the spiked blank was diluted to 125 ml with dichloromethane and similarly evaporated and analyzed to check for losses in evaporating the cleaned extract.

Results and discussion--The results of recovery determinations for the extractable spiking compounds through GPC cleanup and extract concentration are shown in Table 38. Analyte recoveries from Kuderna-Danish concentration were excellent. Recoveries from GPC were good for all compounds except bis(2-chloroethyl)ether. Low recoveries are frequently observed for this compound, bis(2-chloroisopropyl)ether, and benzidine because their poor chromatography makes determination difficult. The lower recovery for bis(2-ethylhexyl)-phthalate reflects the selection of the dump-collect split to achieve effective cleanup.

TABLE 37. ELUTION VOLUMES FOR CORN OIL, PHTHALATES, AND PHENOLS ON GPC USING VARIOUS GELS AND SOLVENTS

Eluent	Compound	Elution volume (ml) LH-20	SX-2	SX-3	SX-4	SX-8
Dichloromethane	Corn oil	50-120	60-170	50-125	50-120	50-95
	Butylbenzylphthalate	80-120	60-170	105-145	92-120	65-80
	Phenols[a]	112-137	120-220	145-195	117-170	110-130
15% Cyclohexane in dichloromethane	Corn oil	65-145	50-160	45-135	40-110	65-135
	Butylbenzylphthalate	85-130	120-175	85-165	85-125	85-130
	Phenols	130-155	160-220	b	135-145	130-155
50% Cyclohexane in dichloromethane	Corn oil	50-115	50-175	45-145	45-120	70-140
	Butylbenzylphthalate	50-100	130-195	100-150	90-130	100-150
	Phenols	90-110	175-245	145-225	135-200	b
50% Acetone in dichloromethane	Corn oil	b	b	b	100-175	b
	Butylbenzylphthalate	b	b	b	110-155	b
	Phenols	b	b	b	110-150	b

a Phenol, 2,4-dichlorophenol, and pentachlorophenol.

b No determination.

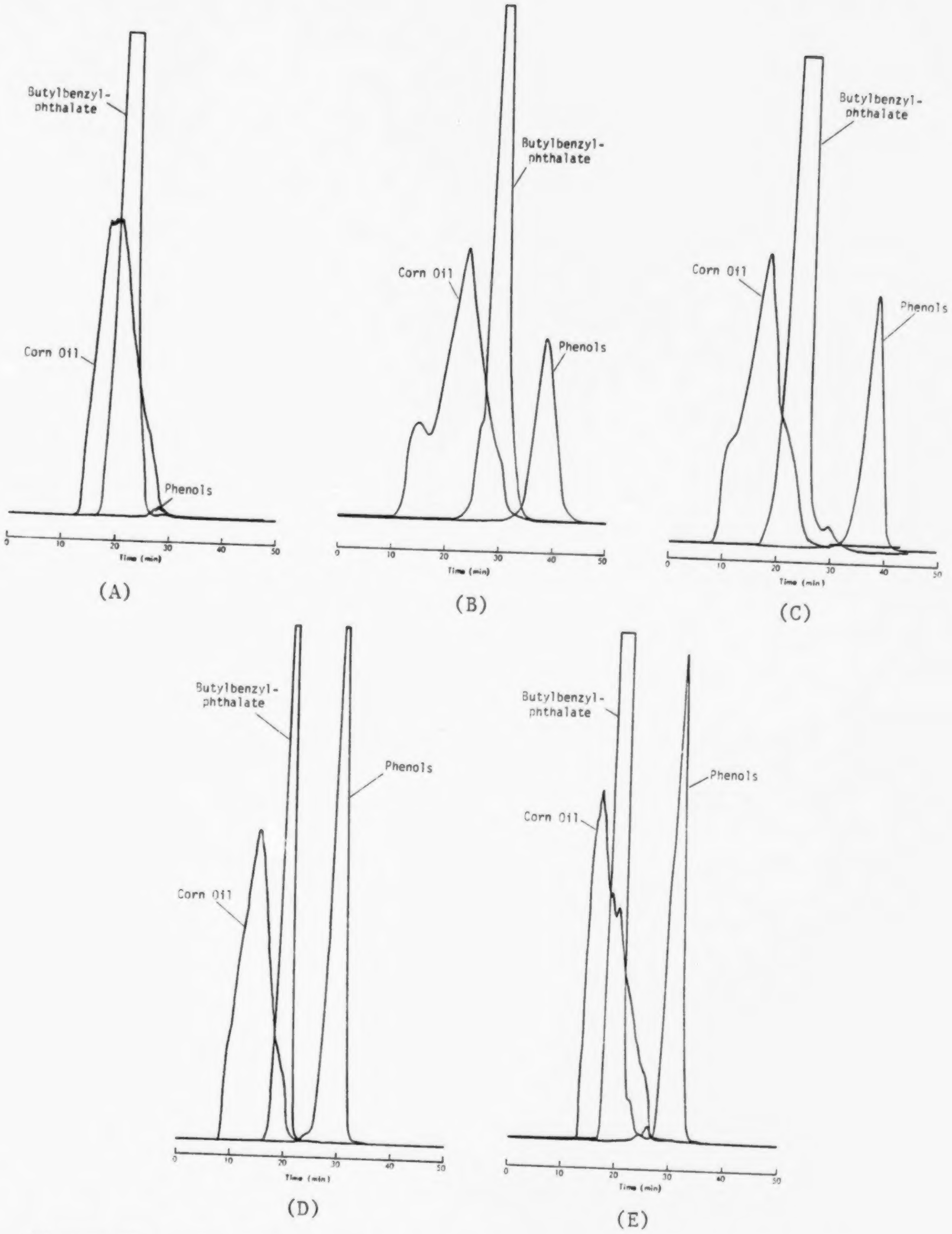
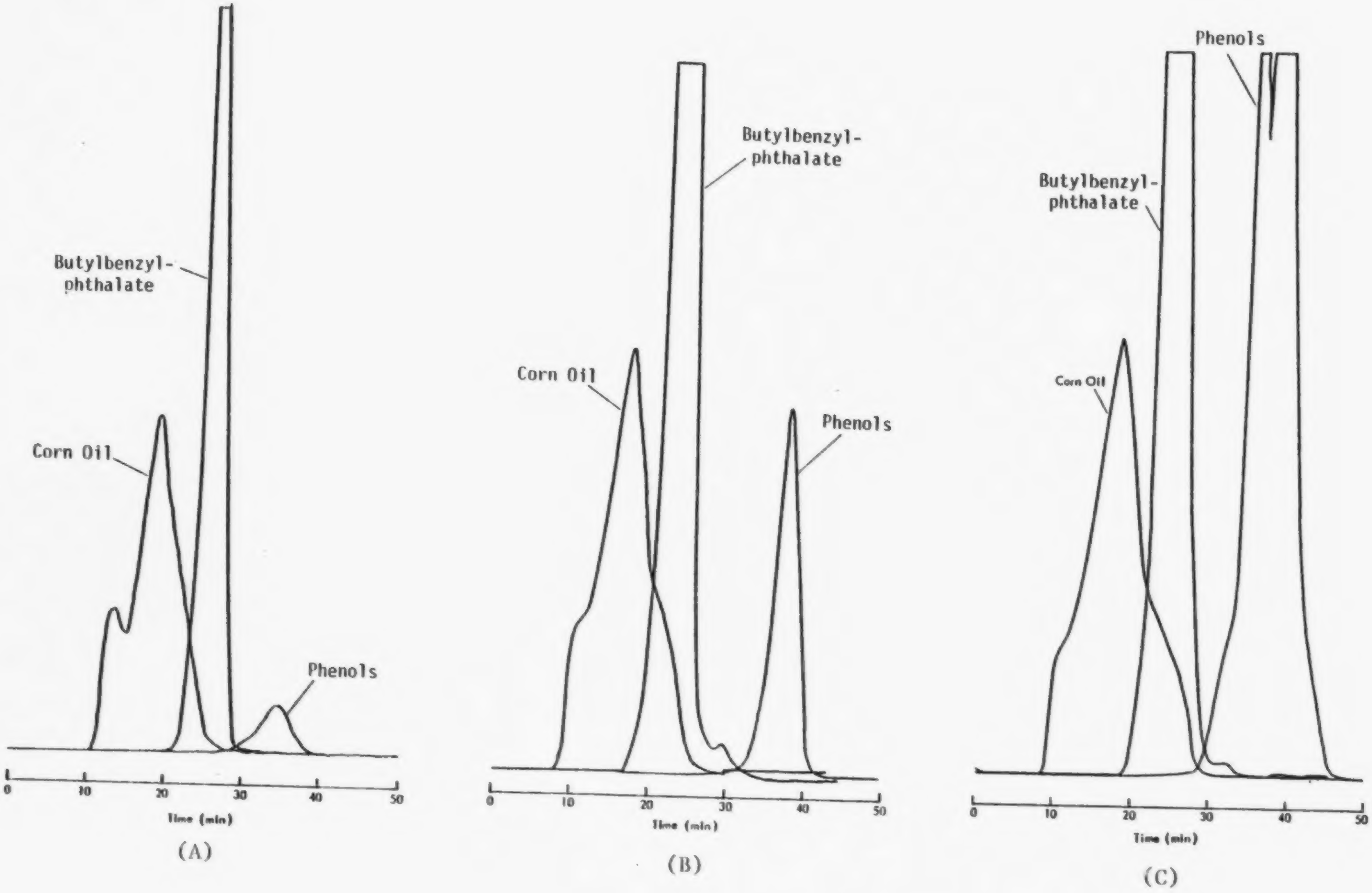


Figure 29. GPC chromatograms on Sephadex LH-20 (A) and Bio-Beads SX-2 (B), SX-3 (C), SX-4 (D), and SX-8 (E) eluted with 15% cyclohexane in dichloromethane.



(A)

(B)

(C)

Figure 30. GPC chromatograms on Bio-Beads SX-3 eluted with dichloromethane (A), 15% cyclohexane in dichloromethane (B), and 50% cyclohexane in dichloromethane (C).

TABLE 38. RECOVERIES OF EXTRACTABLE COMPOUNDS

Compound	Spike level (μg)	% Recovery: GPC cleanup + Kuderna-Danish concentration	% Recovery: Kuderna-Danish concentration
1,4-Dichlorobenzene	100	69	98
Hexachloroethane	100	70	100
Bis(2-chloroisopropyl) ether	100	63	85
Bis(2-chloroethyl) ether	100	37	103
Acenaphthylene	100	77	100
2,6-Dinitrotoluene	100	77	106
Fluoranthene	100	87	98
Benzidine	100	52	103
3,3'-Dichlorobenzidine	100	79	103
n-Butylbenzylphthalate	100	81	104
Bis(2-ethylhexyl)phthalate	100	57	110
Benzo[a]pyrene	100	79	108
Phenol	100	81	101
2,4-Dimethylphenol	100	90	94
2,4-Dichlorophenol	100	86	102
Pentachlorophenol	100	105	100

Absorption Chromatography on Florisil and Silica Gel--

Absorption chromatography on florisil or silica gel is a widely used extract cleanup procedure based on polarity discrimination. The activity of the adsorbent can be adjusted to meet the requirements of a particular analytical system by adding a small amount of water to deactivate a dry, i.e., fully activated, adsorbent. Florisil and silica gel are two of the most widely used adsorbents. A typical adsorption chromatography procedure uses 20 g of adsorbent in a 1- to 25-cm ID column. The sample extract is introduced onto the column in a small volume and the column is eluted with a series of solvents and solvent mixtures with increasing polarities. The first fraction, typically a hydrocarbon solvent, elutes aliphatic hydrocarbons which are discarded. The polarities of the subsequent eluents and the volumes used are designed to elute the analytes while leaving more polar coextractants on the column. Since small amounts of water in the extract partially deactivate the adsorbent and very polar materials remain on the column after analyte elution, the adsorbent is discarded after a single usage.

Adsorption chromatography could be useful for sludge extract cleanup alone or as a supplement to GPC cleanup. Florisil or silica gel provides removal of both aliphatic hydrocarbons and low molecular weight polar compounds which are not removed by GPC. Although florisil and silica gel also remove high molecular weight polar compounds, precleaning with GPC could make removal of these compounds more efficient by reducing the capacity required of the adsorbent.

Partially deactivated florisil and silica gel were evaluated for adsorption chromatographic cleanup of sludge extracts. The elution properties for the extractable spiking compounds were determined and an appropriate elution scheme was developed. Recoveries were determined for the analytes spiked into homogenization/centrifugation extracts both with and without GPC precleanup. Extracts from both 80- and 160-ml sludge aliquots were spiked and chromatographed to test the capacity of the method.

Development of an elution scheme--

Experimental--Florisil (60/100 mesh, Floridin) was cleaned by a 16-h Soxhlet extraction with dichloromethane. The solvent was allowed to evaporate from the adsorbent at ambient temperature prior to activating overnight at 140°C. The clean, active adsorbent was stored at 140°C. Immediately prior to use, the active florisil was deactivated with 1% water (by weight) and was allowed to equilibrate for 4 h, with tumbling. Silica gel (Silica Woelm, 70/150 mesh, ICN) was similarly cleaned, activated, and stored. The silica gel was deactivated with 3% water (by weight) and allowed to equilibrate 4 h, with tumbling prior to use. Columns were prepared by pouring 20 g of the adsorbent into a 28 cm x 2 cm ID glass column half filled with hexane. After allowing the adsorbent to settle in the column, the hexane level was lowered to just above the adsorbent.

The elution characteristics of the extractable spiking compounds on the florisil column were investigated by chromatographing 1.0-ml aliquots of hexane spiked with 27-50 µg of the B/N and acidic compounds. The elution characteristics of B/N spiking compounds on the silica gel column were similarly investigated. Since preliminary experiments indicated that significant quantities of 1,4-dichlorobenzene and hexachloroethane were eluted from silica gel with 50 ml of hexane, the initial fraction (Fraction I) was eluted with only 20 ml of hexane. Subsequent fractions were eluted with 50 ml each of 10% dichloromethane in hexane (Fraction II) and 50% dichloromethane in hexane (Fraction III), followed by 150 ml of 5% acetone in dichloromethane (Fraction IV). The fractions eluted were concentrated to 1.0 ml in Kuderna-Danish evaporators and the analytes determined by GC/FID using the preliminary POTW protocol chromatographic methods.

Results and discussion--The recoveries for the spiked extractable compounds in each fraction eluted from the florisil and silica gel columns are shown in Tables 39 and 40, respectively. The distributions of the B/N compounds within the fraction eluted were very similar for both the florisil and silica gel column. That is, the performances of the florisil and silica gel columns were roughly equivalent.

The recoveries observed for the phenols from the florisil column and for the benzidenes from both columns were low. More polar eluents are likely required to recover these compounds. However, more polar eluents are likely to elute significant quantities of polar coextracting interferences from sludge extracts. Subsequent development of florisil and silica gel extract cleanup methods was focused on the B/N compounds only.

Recoveries from spiked sludge extracts--Recoveries were determined for B/N compounds spiked into extracts prepared from 80- and 160-ml aliquots of combined POTW sludge and cleaned up by florisil and silica gel chromatography. This study was designed to test both the recoveries and cleanup capacities of the columns. In addition, recoveries were determined for extracts spiked following GPC cleanup to investigate the possible enhancement of the performance of adsorption chromatographic cleanup by removing high molecular weight biogenic compounds.

Experimental--Homogenization/centrifugation extracts were prepared from 80- and 160-ml aliquots of combined POTW sludge. Half of all extracts were cleaned by GPC, and all extracts were concentrated to 5 to 10 ml. Selected extracts were spiked with the B/N spiking compounds. Extracts prepared from 160-ml sludge aliquots were spiked at twice the levels for extracts from 80-ml aliquots. All combinations of spiked and unspiked extracts with and without GPC cleanup were chromatographed on florisil and silica gel columns. The extracts were loaded onto the columns by mixing with 2 g of the adsorbent, removing the solvent under a gentle stream of dry nitrogen, and then transferring the adsorbed extract to the top of the column for elution. The columns were eluted in four fractions as described above. Fraction I (20 ml hexane) was discarded. Fractions II, III, and IV were composited or analyzed separately for some extracts. All composited fractions (II through IV) and individual fractions were concentrated and analyzed by GC/MS using the procedures described in the preliminary POTW protocol.

TABLE 39. RECOVERIES OF EXTRACTABLE COMPOUNDS FROM SPIKED BLANK EXTRACTS BY FLORISIL CHROMATOGRAPHY ELUTED WITH HEXANE, DICHLOROMETHANE AND ACETONE

Compound	Spike level (μg)	% Recovery				
		Fraction I[a]	Fraction II[b]	Fraction III[c]	Fraction IV[d]	Total
1,4-Dichlorobenzene	46.8	0	65	5.1	2.4	73
Hexachloroethane	31.2	0	70	2.6	0.6	73
Bis(2-chloroisopropyl)ether	49.7	0	0	20	41	61
Bis(2-chloroethyl)ether	31.7	0	0	3.8	29	33
Acenaphthylene	28.5	0	14	37	13	65
2,6-Dinitrotoluene	35.1	0	0	0	49	49
Fluoranthene	27.0	0.2	0.1	43	25	68
Benzidine	31.0	0	0	0	0	0
3,3'-Dichlorobenzidine	36.4	0	0	0	0	0
n-Butylbenzylphthalate	45.2	0.9	0	0	0.5	1.4
Bis(2-ethylhexyl)phthalate	39.6	0	0	6.1	0	6.1
Benzo[a]pyrene	30.0	0	0	8.1	22	30
Phenol	48.4	0	0	3.1	12	16
2,4-Dimethylphenol	35.4	0	7.1	11	11	29
2,4-Dichlorophenol	32.8	0	1.4	7.4	31	40
Pentachlorophenol	30.4	0	0	0	0	0

[a] Fraction I was eluted with 20 ml hexane.

[b] Fraction II was eluted with 50 ml 10% dichloromethane in hexane.

[c] Fraction III was eluted with 50 ml 50% dichloromethane in hexane.

[d] Fraction IV was eluted with 150 ml 5% acetone in dichloromethane.

TABLE 40. RECOVERIES OF BASE/NEUTRAL COMPOUNDS FROM SPIKED BLANK EXTRACTS BY SILICA GEL CHROMATOGRAPHY ELUTED WITH HEXANE, DICHLOROMETHANE AND ACETONE

Compound	Spike level (μg)	% Recovery				
		Fraction I[a]	Fraction II[b]	Fraction III[c]	Fraction IV[d]	Total
1,4-Dichlorobenzene	46.8	0	62	8	0	70
Hexachloroethane	31.2	0	83	0	0	83
Bis(2-chloroisopropyl)ether	49.6	0	0	0	85	85
Bis(2-chloroethyl)ether	31.6	0	0	0	93	93
Acenaphthylene	28.5	0	0	79	0	79
2,6-Dinitrotoluene	35.1	0	0	0	96	96
Fluoranthene	27.0	0	0	90	0	90
Benzidine	31.0	0	0	0	0	0
3,3'-Dichlorobenzidine	36.4	0	0	0	50	50
n-Butylbenzylphthalate	45.2	0	0	0	97	97
Bis(2-ethylhexyl)phthalate	39.6	0	0	0	93	93
Benzo[a]pyrene	30.0	0	0	79	0	78

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[a] Fraction I was eluted with 20 ml hexane.

[b] Fraction II was eluted with 50 ml 10% dichloromethane in hexane.

[c] Fraction III was eluted with 50 ml 50% dichloromethane in hexane.

[d] Fraction IV was eluted with 150 ml 5% acetone in dichloromethane.

Results and discussion--Table 41 shows a sample of the recoveries observed for spiked sludge extracts. This table shows the results for extracts from replicate 80-ml aliquots of combined sludge, spiked without GPC cleanup, and chromatographed on florisil. Recoveries observed were generally good and fairly reproducible for all compounds except benzidene.

The distribution of analytes among Fractions II, III, and IV is very similar to that for the spiked blank shown in Table 41. The distribution of compounds among the fractions could be helpful in cases where determination of selected compounds is required. A significant portion of the background material in the composite of Fractions II to IV was contributed by Fraction II. The GC/MS chromatograms for the composite of Fractions II to IV for the experiment represented in Table 41 are shown in Figure 31. Figures 32 to 34 show the GC/MS chromatograms for the individual fractions. These chromatograms indicate that determination of compounds eluting in Fractions III and IV would be easier if those fractions were analyzed separately.

The recoveries obtained for spiked compounds in replicate extracts from 80- and 160-ml sludge aliquots with and without GPC chromatographed on florisil and silica gel are summarized in Table 42. The recoveries observed for the florisil and silica gel columns were similar. Recoveries were also similar for extracts with and without GPC cleanup. The GC/MS chromatogram for the composite of Fractions II through IV for a spiked 80-ml sludge aliquot cleaned by GPC is shown in Figure 35. The background in this chromatogram is very similar to that for a replicate extract without GPC (Figure 31).

The recoveries observed for extracts prepared from 80- and 160-ml sludge aliquots are comparable. However, the florisil-cleaned extracts of 160-ml sludge aliquots had to be analyzed at a larger final extract volume to avoid overloading the GC/MS detection system. Hence, no real gain in method sensitivity was realized by extracting larger sludge aliquots.

Adsorption on Cesium Silicate--

The use of cesium silicate has been reported for isolation of phenolics from neutral compounds in dilute wastewater extracts.[12,13] This procedure was evaluated as a cleanup method for sludge extracts. Recoveries were determined for spiked blanks and then for spiked sludge extracts.

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[12] Stalling, D. L., L. M. Smith and J. D. Petty. Approaches to Comprehensive Analyses of Persistent Halogenated Environmental Contaminants. Measurement of Organic Pollutants in Water and Wastewater. ASTM STD 686, C. E. Van Hall, Ed., 1979, pp. 302-323.

[13] DeWalle, F. and E. Chian. Presence of Priority Pollutants in Sewage and Their Removal in Sewage Treatment Plants. First Annual Report to EPA, Grant No. R806102, 1979.

TABLE 41. RECOVERIES OF BASE/NEUTRAL COMPOUNDS FROM SPIKED SLUDGE EXTRACTS BY FLORISIL CHROMATOGRAPHY, WITHOUT CLEANUP BY GPC, ELUTED WITH HEXANE, DICHLOROMETHANE, AND ACETONE

Compound	Spike level (μg)	Unspiked sludge level (μg)	Spiked sludge 1		Spiked sludge 2				Average recovery (%)
			Fraction[a] II-IV (μg)	Total recovery (%)	Fraction II[b] (μg)	Fraction III[c] (μg)	Fraction IV[d] (μg)	Total recovery (%)	
1,4-Dichlorobenzene	46.8	33	60	58	70	0	0	29	68
Hexachloroethane	31.2	0	30	96	38	0	0	123	110
Bis(2-chloro-isopropyl)ether	149.0	0	190	128	0	0	105	70	99
Bis(2-chloro-ethyl)ether	95.0	0	297	313[e]	0	70	74	74	74
Acenaphthylene	28.5	0	33	116	0	21	0	75	96
2,6-Dinitrotoluene	35.1	0	54	154	0	0	31	89	122
Fluoranthene	27.0	7	29	81	0	24	2	70	75
Benzidine	93.0	0	0	0	0	0	0	0	0
3,3'-Dichloro-benzidine	109.2	0	96	88	0	0	99	93	90
n-Butylbenzyl-phthalate	45.0	196	243	104	0	0	235	113	108
Bis(2-ethylhexyl)-phthalate	39.6	134	148	35	0	0	157	62	48
Benzo[a]pyrene	30.0	0	15	50	0	9	7	53	52

[a] Fraction II-IV is the combined eluent obtained by elution with 50 ml 10% dichloromethane in hexane, 50 ml 50% dichloromethane in hexane, and 150 ml 5% acetone in dichloromethane.

[b] Fraction II was eluted with 50 ml 10% dichloromethane in hexane.

[c] Fraction III was eluted with 50 ml 50% dichloromethane in hexane.

[d] Fraction IV was eluted with 150 ml 5% acetone in dichloromethane.

[e] Anomalous recovery for sludge extract 1 not averaged.

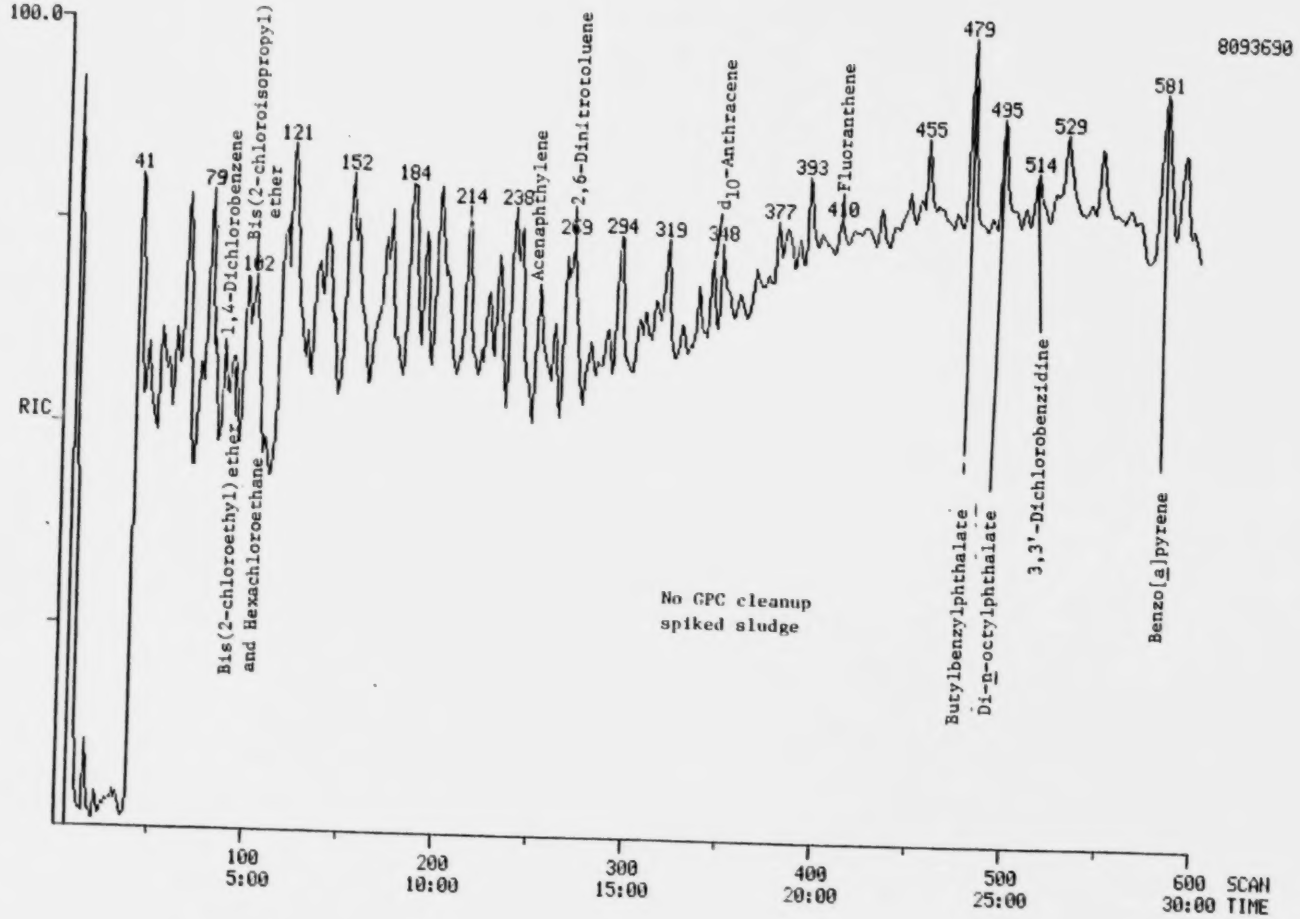

Figure 31. GC/MS chromatogram of the combined eluent (Fractions II-IV) obtained by florisil cleanup of the spiked sludge (no GPC cleanup).

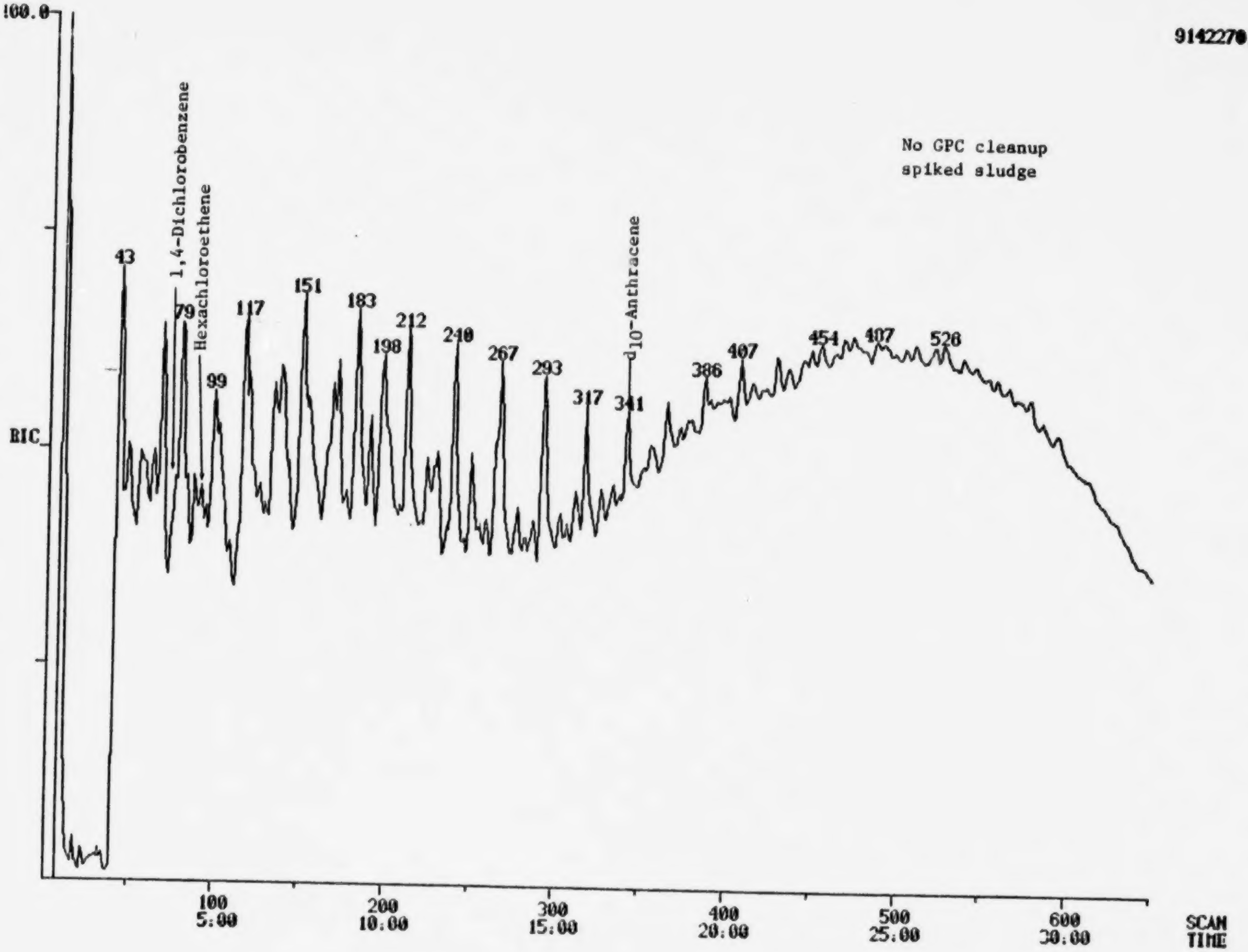

Figure 32. GC/MS chromatogram of Fraction II obtained by florisil cleanup of the spiked sludge (no GPC cleanup).

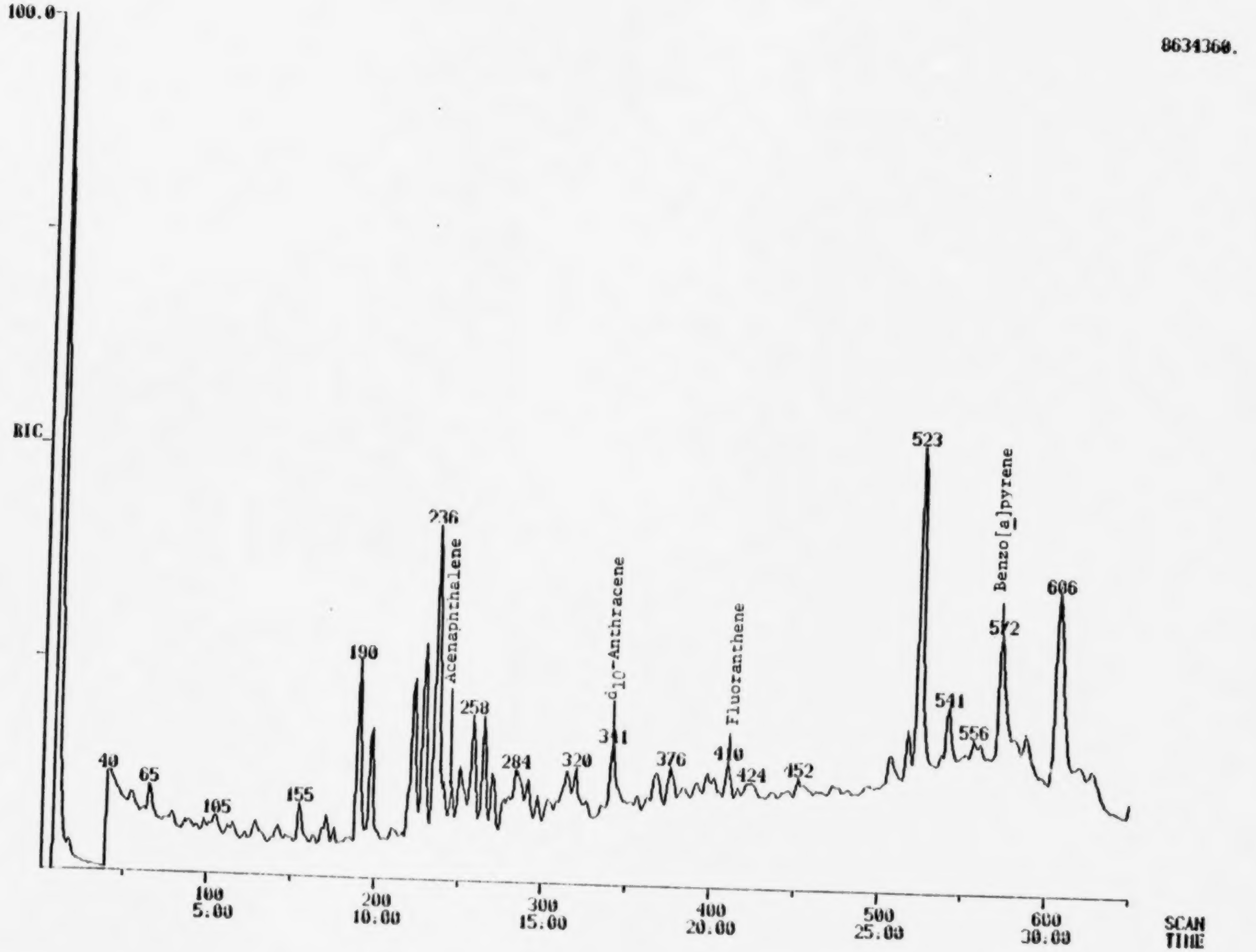

Figure 33. GC/MS chromatogram of Fraction III obtained by florisil cleanup of the spiked sludge (no GPC cleanup).

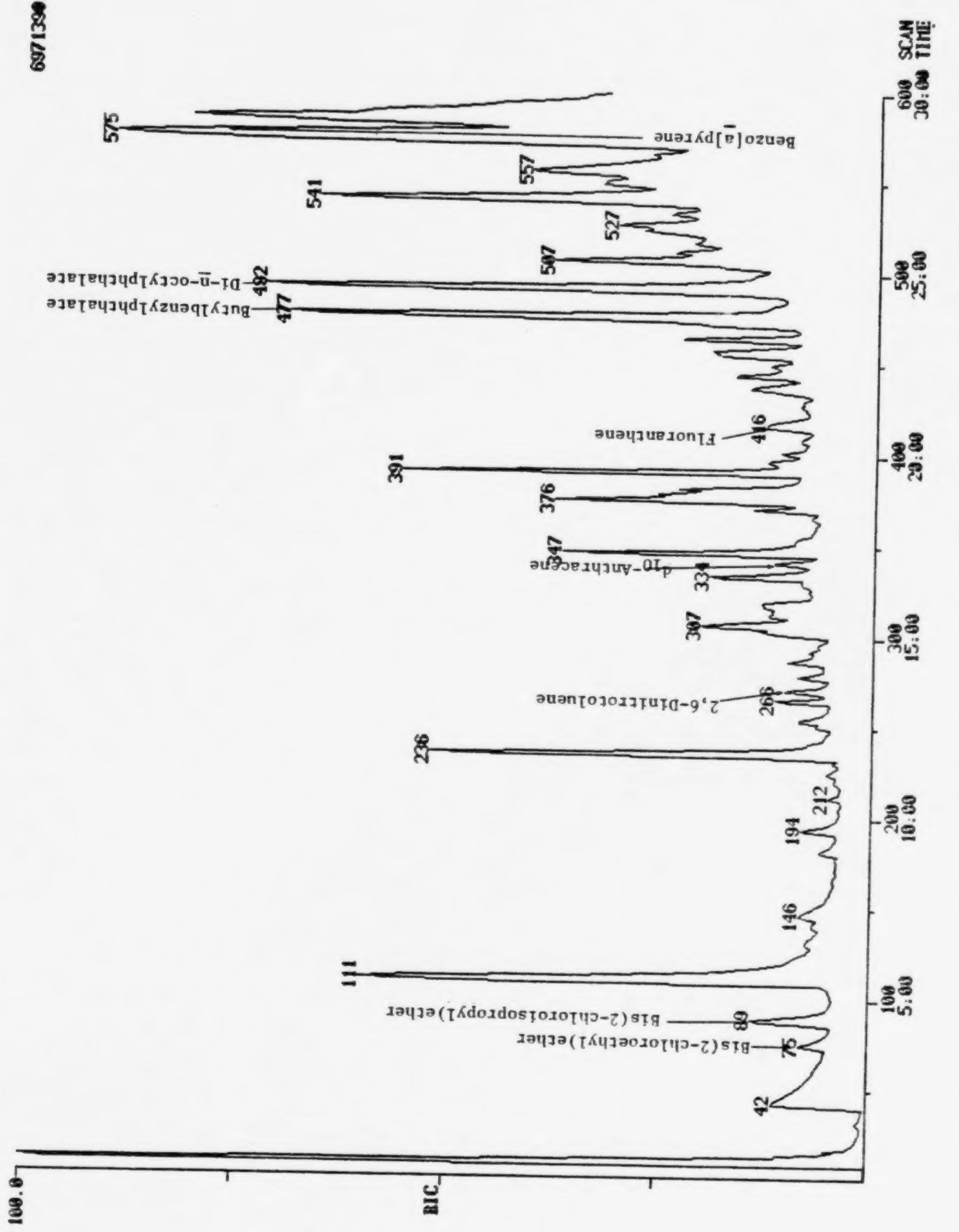

Figure 34. GC/MC chromatogram of Fraction IV obtained by florisil cleanup of the spiked sludge (no GPC cleanup).

TABLE 42. SUMMARY OF RECOVERIES FOR THE EXTRACTABLE COMPOUNDS FROM EXTRACTS OF 80- AND 160-ml SLUDGE ALIQUOTS SPIKED AND THEN CLEANED WITH FLORISIL OR SILICA GEL

Compound	Spike level (μg)		Average recovery (%)[a]							
			Florisil				Silica gel			
			With GPC		Without GPC		With GPC		Without GPC	
	80 ml	160 ml	80 ml	160 ml	80 ml	160 ml	80 ml	160 ml	80 ml	160 ml
1,4-Dichlorobenzene	47	94	92	142	68	88	73	109	62	95
Hexachloroethane	31	62	79	97	110	70	95	54	116	47
Bis(2-chloroisopropyl)ether	149	298	100	102	99	111	102	112	129	62
Bis(2-chloroethyl)ether	95	190	103	49	74	53	85	66	116	93
Acenaphthylene	29	57	97	148	96	109	87	72	91	93
2,6-Dinitrotoluene	35	70	90	110	122	139	108	102	129	108
Fluoranthene	27	54	85	110	75	135	69	55	98	103
Benzidine	93	186	17	0	0	0	0	0	0	0
3,3-Dichlorobenzidine	109	218	106	168	90	167	63	155	70	1
n-Butylbenzylphthalate	45	90	170	b	108	b	148	b	103	b
Bis(2-ethylhexyl)phthalate	40	80	152	b	48	b	108	b	270	b
Benzo[a]pyrene	30	60	52	155	52	130	47	114	81	99

[a] Average of two determinations.

[b] Recoveries were not determined because the levels in the unspiked extracts were much higher than the spike level.

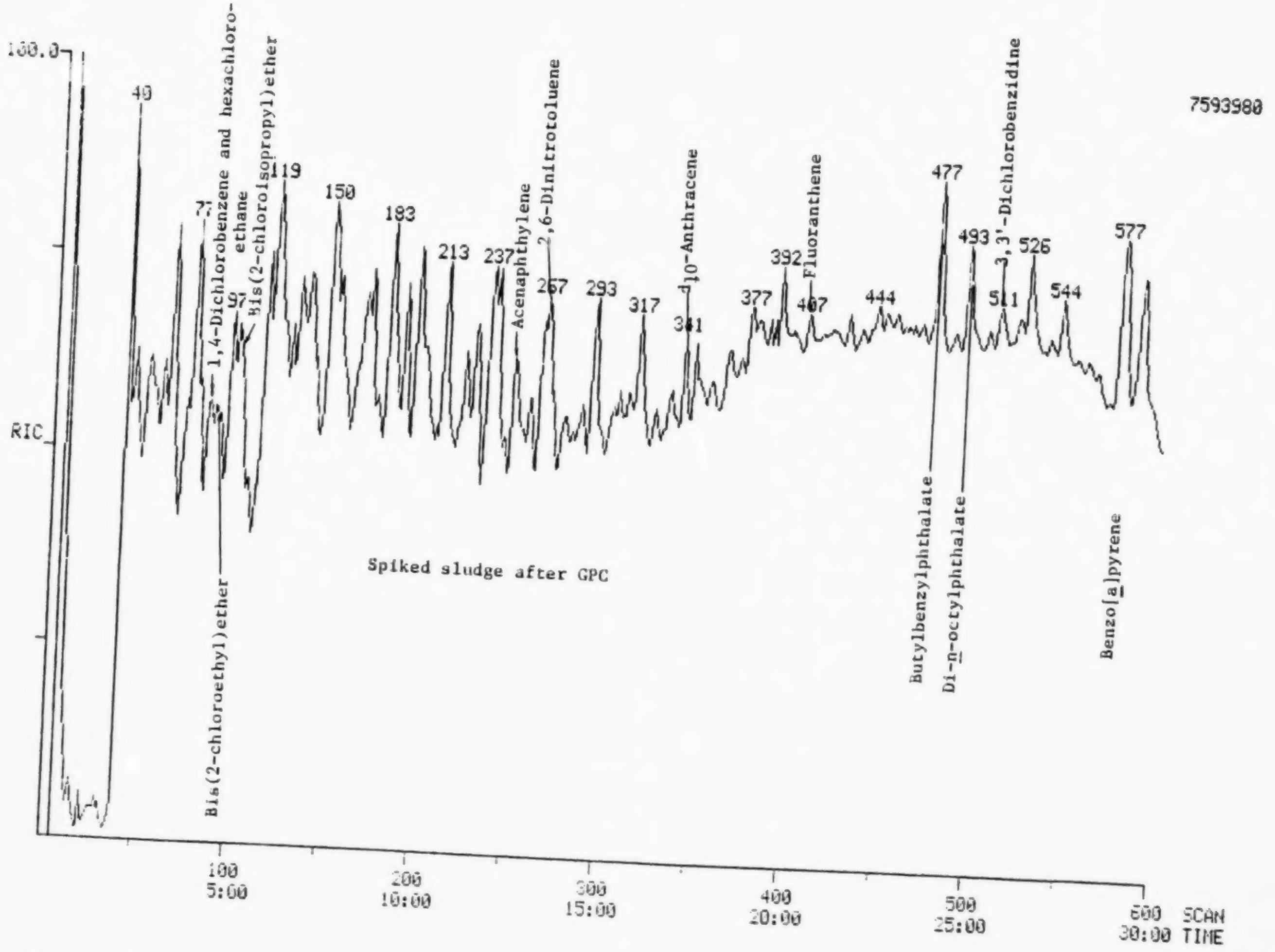

Figure 35. GC/MS chromatogram of combined eluent (Fraction II-IV) obtained by florisil cleanup of the spiked sludge following GPC cleanup.

Recoveries from spiked blank extracts--

Experimental--Cesium silicate was prepared by procedures reported by DeWalle and Chian.[13] Two hundred grams of silica gel (Davidson 923, 100/120 mesh) were added to 600 ml of a saturated solution of cesium hydroxide in methanol. The mixture was stirred at room temperature for 1 hr, was allowed to settle, and the supernatant was decanted. The residue was filtered and the filtrate was washed with 250 ml of methanol followed by 250 ml of dichloromethane. The adsorbent was dried and stored at 140°C. Columns were prepared by adding 20 g of cesium silicate into a 280 cm x 2 cm ID column half filled with dichloromethane. The adsorbent was allowed to settle and the solvent level was adjusted to just above the adsorbent. A dilute, spiked blank was prepared by spiking a 150-ml aliquot of dichloromethane with the acidic spiking compounds. The spiked blank was allowed to pass through the column at 3 ml/min and the eluent was collected (Fraction I). The column was then eluted with 20 ml of methanol (Fraction II) and 100 ml of methanol (Fraction III). Since cesium silicate has some appreciable solubility in methanol, the methanol eluents were concentrated to 4 ml in Kuderna-Danish evaporators and then were partitioned between 6 ml of water (adjusted to pH 1) and 2 ml of dichloromethane. The dichloromethane fraction was removed and the aqueous fraction was extracted with two additional 2-ml aliquots of dichloroethane. All three extracts were composited. The dichloromethane column eluent (Fraction I) and the methanol extracts (Fractions II and III) were concentrated to 1.0 ml, and the analytes were determined by GC/FID using the chromatographic conditions described in the preliminary POTW sludge protocol.

Results and discussion--The results of recovery determinations for a spiked blank are shown in Table 43. No breakthrough of the analytes was observed, i.e., none of the spiked phenols were found in Fraction I. It was also determined that 20 ml of methanol was sufficient to elute the spiked phenols from the column.

Recoveries from spiked sludge extracts--Recoveries were determined for spiked compounds in an extract from an 80-ml aliquot of sludge. Recoveries were also determined for spiked extracts from 160-ml aliquots of a different sludge with and without GPC cleanup.

Experimental--Two extracts were prepared from 80-ml aliquots of sludge and were spiked with the acidic spiking compounds. Both dilute extracts (240 ml) were passed through the column at 3 ml/min. The columns were eluted with 50 ml of methanol and the methanol eluents were back extracted as described in the preceding section. Spiked and unspiked extracts of 160-ml sludge aliquots with and without GPC cleanup were processed on cesium silicate columns in the same manner except that the original extract eluents were collected. All fractions were concentrated and analyzed by GC/MS with the procedures described in the preliminary POTW sludge protocol.

TABLE 43. RECOVERIES OF ACIDIC COMPOUNDS FROM SPIKED BLANK EXTRACTS BY CESIUM SILICATE CHROMATOGRAPHY

	Spiked blank				
Compound	Spike level (μg)	Fraction I[a] (μg)	Fraction II[b] (μg)	Fraction III[c] (μg)	% Recovery
Phenol	48.4	0	39.5	0	82
2,4-Dimethylphenol	35.4	0	23.7	0	67
2,4-Dichlorophenol	32.8	0	26	0	79
Pentachlorophenol	30.4	0	37	0	122

[a] Fraction I represents the dichloromethane eluate.

[b] Fraction II was eluted with 20 ml methanol.

[c] Fraction III was eluted with 100 ml methanol.

Results and discussion--The results of recovery determinations for spiked compounds from sludge extracts are shown in Table 44. The recoveries observed for the extract of 80-ml aliquots of sludge were good. The very high recoveries noted for phenol and pentachlorophenol in the extracts of 160-ml sludge aliquots remain unexplained. However, significant portions of the analytes spiked into these extracts eluted with the extract (Fraction I). The breakthrough is probably due to the higher levels of coextracted materials blocking the adsorption sites on the cesium silicate. Since the results were no better for extracts that had been cleaned by GPC, the interferences are likely low molecular weight compounds. Hence, the cleanup capacity of cesium silicate may be somewhat limited.

Method Selection--

The GPC extract cleanup method used in the preliminary POTW sludge protocol, which consisted of Bio-Beads SX-3 eluted with dichloromethane, provided the best combination of peak shape and separation between corn oil (used to simulate high molecular weight biogenic interferences) and butylbenzylphthalate (one of the largest extractable priority pollutants) of the gel-solvent combinations tested. Good recoveries were observed for compounds in spiked blanks processed by this GPC procedure. This molecular size based discrimination was shown to be applicable for cleaning both acidic and B/N extracts.

Adsorption chromatography on florisil and silica gel provided good cleanup and recoveries for B/N compounds. Recoveries for the acidic compounds was poor. The florisil and silica gel procedures evaluated provided roughly equivalent recoveries. No improvement in the performance of these procedures was realized for extracts precleaned by GPC. Although recoveries observed for compounds spiked into extracts from 80- and 160-ml sludge aliquots were very similar, cleaned extracts from 160-ml sludge aliquots had to be analyzed at a larger final volume. Hence, no real improvement in method sensitivity resulted from extracting larger sludge aliquots.

Cesium silicate chromatography provided good recoveries for spiked blanks and spiked extracts from 80-ml sludge aliquots. However, recoveries were poor for compounds spiked into extracts from 160-ml sludge aliquots.

Selection of GPC or florisil or silica gel methods for cleaning B/N extracts should be based on the specific requirements of the sludge extract and the determination method. The polarity based adsorption chromatography procedures provide more effective cleanup for extracts containing significant quantities of low molecular weight polar coextractants. In addition, florisil and silica gel remove aliphatic hydrocarbons. Hence, extracts cleaned by the florisil or silica gel methods are more likely to be amenable to analysis using capillary column GC/MS. On the other hand, the GPC cleanup method can easily be automated and produces extracts suitable for packed column GC/MS. The poor recoveries observed for compounds spiked into extracts from 160-ml sludge aliquots and cleaned with cesium silicate indicated that the column is very susceptible to overloading. Hence, GPC is a more reliable procedure for cleaning acidic extracts.

TABLE 44. RECOVERIES OF ACIDIC COMPOUNDS FROM SPIKED SLUDGE EXTRACTS BY CESIUM SILICATE CHROMATOGRAPHY

	80-ml			160-ml								
					Without GPC				With GPC			
			Recovery		Unspike level		Spike recovery		Unspike level		Spike recovery	
Compound	Spike level (μg)	Unspiked level (μg)	Fraction II[a] (%)	Spike level (μg)	Fraction I[b] (μg)	Fraction II (μg)	Fraction I (%)	Fraction II (%)	Fraction I (μg)	Fraction II (μg)	Fraction I (%)	Fraction II (%)
Phenol	48.4	8.4	68	76.2	18	85	150	62	33	88	120	150
2,4-Dimethylphenol	35.4	ND[c]	75	49.2	ND	ND	68	43	ND	ND	63	33
2,4-Dichlorophenol	32.8	2.8	89	53.1	ND	ND	57	23	ND	ND	51	39
Pentachlorophenol	30.4	9.8	120	45.6	ND	1.7	32	160	ND	0.5	0	180

[a] Eluted with 50 ml of methanol.

[b] The crude extract eluate.

[c] ND = not detected.

GC/MS Procedures

Capillary GC/MS procedures were evaluated as an alternative to the packed column GC/MS methods described in the preliminary POTW sludge protocol. The performances of selected column systems were compared. The column system providing the best overall performance was evaluated with cleaned sludge extracts. Relative retention times and response factors were determined for the B/N and acidic priority pollutants.

Performance Evaluations for Selected Column Systems--

The performances of four wall-coated open tubular (WCOT) capillary columns were evaluated by chromatographing commercially prepared capillary column performance test solutions and solutions of the B/N and acidic spiking compounds. Two columns were evaluated with both nitrogen and hydrogen carrier gases to investigate the influence of the carrier gas on column performance.

Experimental--The WCOT capillary columns evaluated and the operating conditions used in these evaluations are shown in Table 45. The columns were tested in a Varian 3700 chromatograph with a flame ionization detector. This chromatograph was fitted with a Varian Model 1070 split/splitless injection system. Two commercially prepared column performance test solutions were chromatographed on each column. The contents of these test solutions are listed in Table 46. The resulting chromatograms were used to calculate the height equivalent to a theoretical plate (HETP), peak asymmetries (AS) and column adsorption for selected compounds, and the acid-base character (pH) of the columns. Solutions of the acidic and B/N spiking compounds were also chromatographed on each column system. The amount injected for each compound ranged 50 to 100 ng for the B/Ns and 75 to 125 ng for the acids.

Results and discussion--Sample chromatograms obtained for performance evaluation test mixtures on each column are shown in Figures 36 to 39. The results of the column performance parameters determined are shown in Table 47. The HETP for each column was calculated as a measure of the resolving power according to the formula:

$$\text{HETP} = \frac{L}{N_{eff}}$$

where L is the column length and N_{eff} is the number of theoretical plates. N_{eff} is calculated as follows:

$$N_{eff} = 5.545 \left(\frac{t_r'}{W_{0.5}} \right)^2$$

where t_r' is the retention time of the selected compound less the retention time for methane ($t_r - t_m$) and $W_{0.5}$ is the peak width at half height.

TABLE 45. CHROMATOGRAPHIC CONDITIONS USED IN THE EVALUATION OF CAPILLARY COMPOUNDS BY GC/FID

	Column type					
Parameter	SP-2100	Fused silica SP-2100 (Carbowax 208 deactivated)	SE-52	SE-52	Fused silica SE-54	Fused silica SE-54
Column dimensions	0.25 mm ID x 30 m	0.21 mm ID x 25 m	0.24 mm ID x 18 m	0.24 mm ID x 18 m	0.24 mm ID x 15 m	0.24 mm ID x 15 m
Carrier gas	nitrogen	nitrogen	nitrogen	hydrogen	nitrogen	hydrogen
Flow velocity (cm/sec)	17	30	25	25	31	60, 45[a]
Makeup gas (nitrogen) flow (ml/min)	30	30	30	30	30	30
Injector temperature (°C)	300	300	300	300	300	300
Column temperature program:						
Performance check	isothermal at 120°C	isothermal at 100°C	isothermal at 90°C	b	isothermal at 85°C	isothermal at 85°C
Base/neutrals	4 min at 50°C, then to 280°C at 4°C/min	1 min at 50°C, then to 280°C at 4°C/min	50-280°C at 4°C/min	5 min at 40°C, then to 280°C at 10°C/min	4 min at 50°C, then to 280°C at 4°C/min	4 min at 50°C, then to 280°C at 4°C/min
Acids	2 min at 70°C, then to 270°C, at 8°C/min	1 min at 50°C, then to 240°C at 4°C/min	2 min at 45°C, then to 250°C at 10°C/min	b	2 min at 70°C, then to 280°C at 8°C/min	2 min at 70°C, then to 280°C at 8°C/min

a 60 cc/sec for base/neutral runs and 45 cm/sec for acid runs.

b Not tested with this solution.

TABLE 46. COMPOSITION OF CAPILLARY COLUMN PERFORMANCE TEST MIXTURES

Test mixture	Composition	
Varian P/N 82-005049-01 (nonpolar)	2-octanone	0.2 μg/μl
	1-octanol	0.2
	naphthalene	0.2
	2,6-dimethylphenol	0.2
	2,4-dimethylaniline	0.2
	C_{12}-alkane	0.2
	C_{13}-alkane	0.2
Alltech TP-5 (polar)	C_{13}-alkane	0.1 μg/μl
	C_{14}-alkane	0.1
	C_{15}-alkane	0.1
	C_{16}-alkane	0.1
	1-octanol	0.5
	5-nonanone	0.3
	2,6-dimethylaniline	0.4
	2,6-dimethylphenol	0.4
	naphthalene	0.5

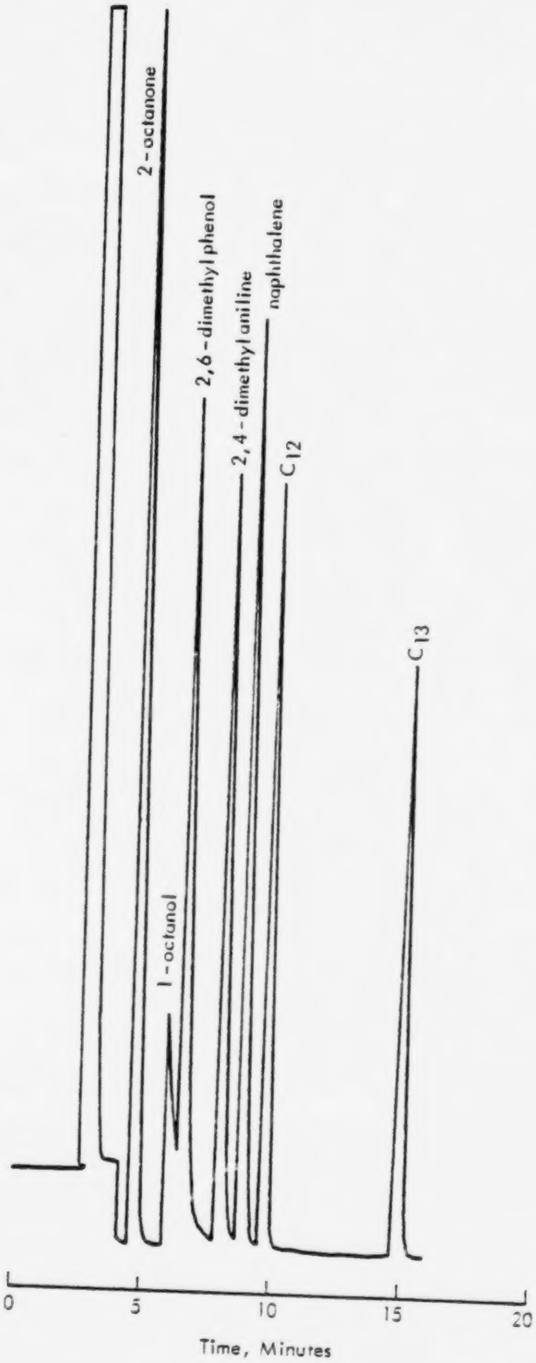

Figure 36. HRGC/FID chromatogram of a performance test solution on the SP-2100 capillary column.

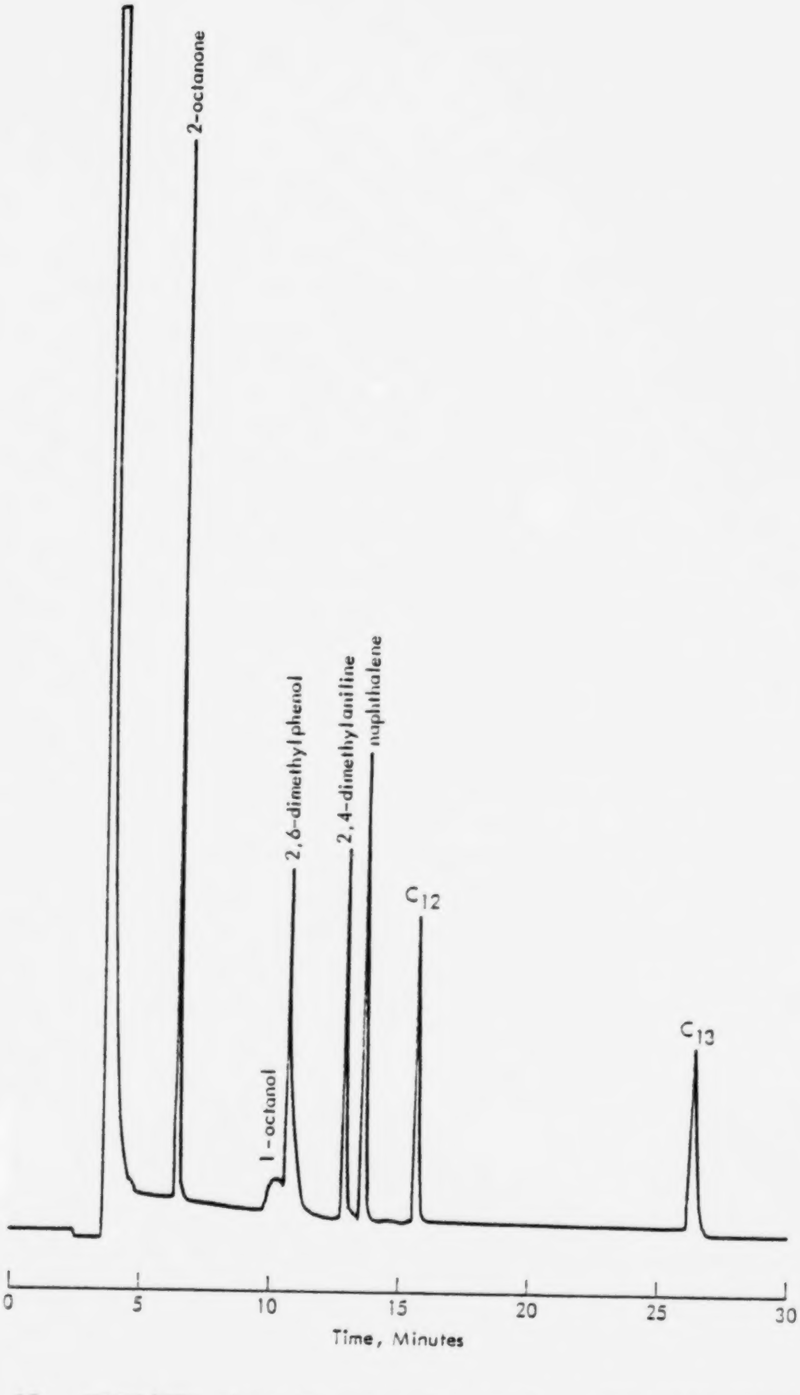

Figure 37. HRGC/FID chromatogram of a performance test solution on the fused silica SP-2100 (Carbowax 20M deactivated) capillary column.

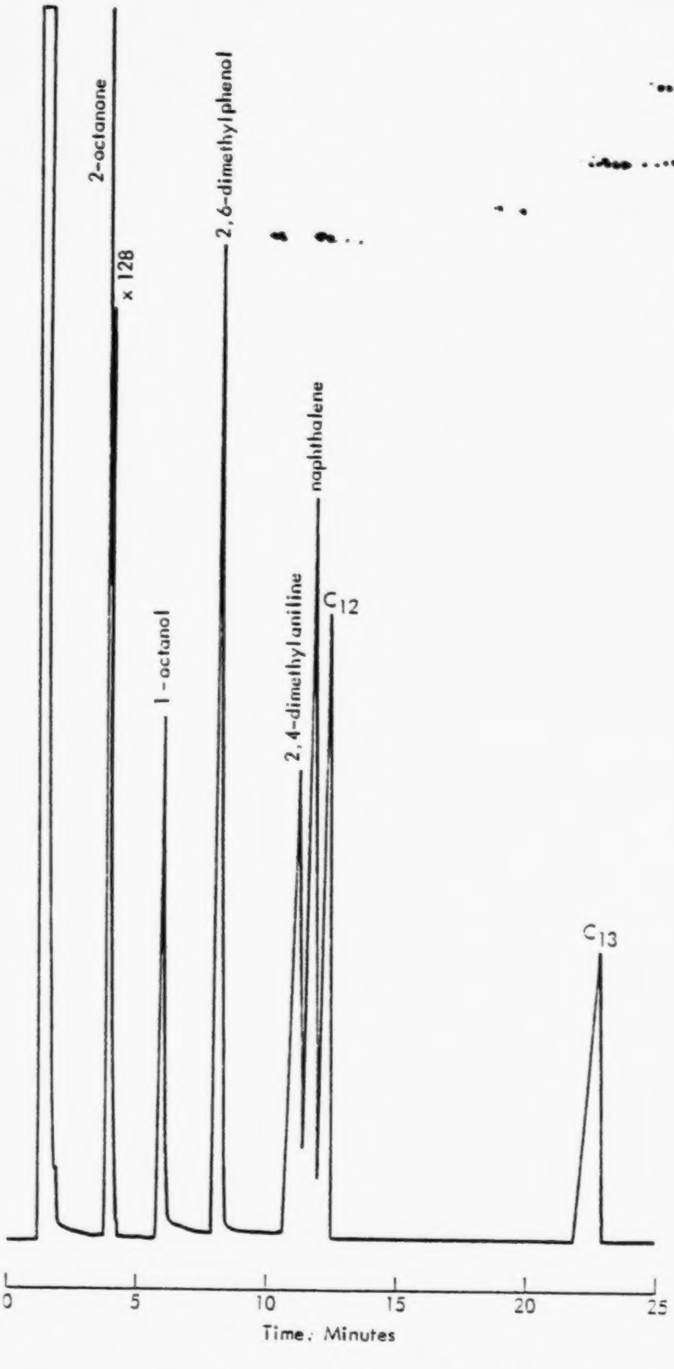

Figure 38. HRGC/FID chromatogram of a performance test solution on the SE-52 capillary column eluted with nitrogen.

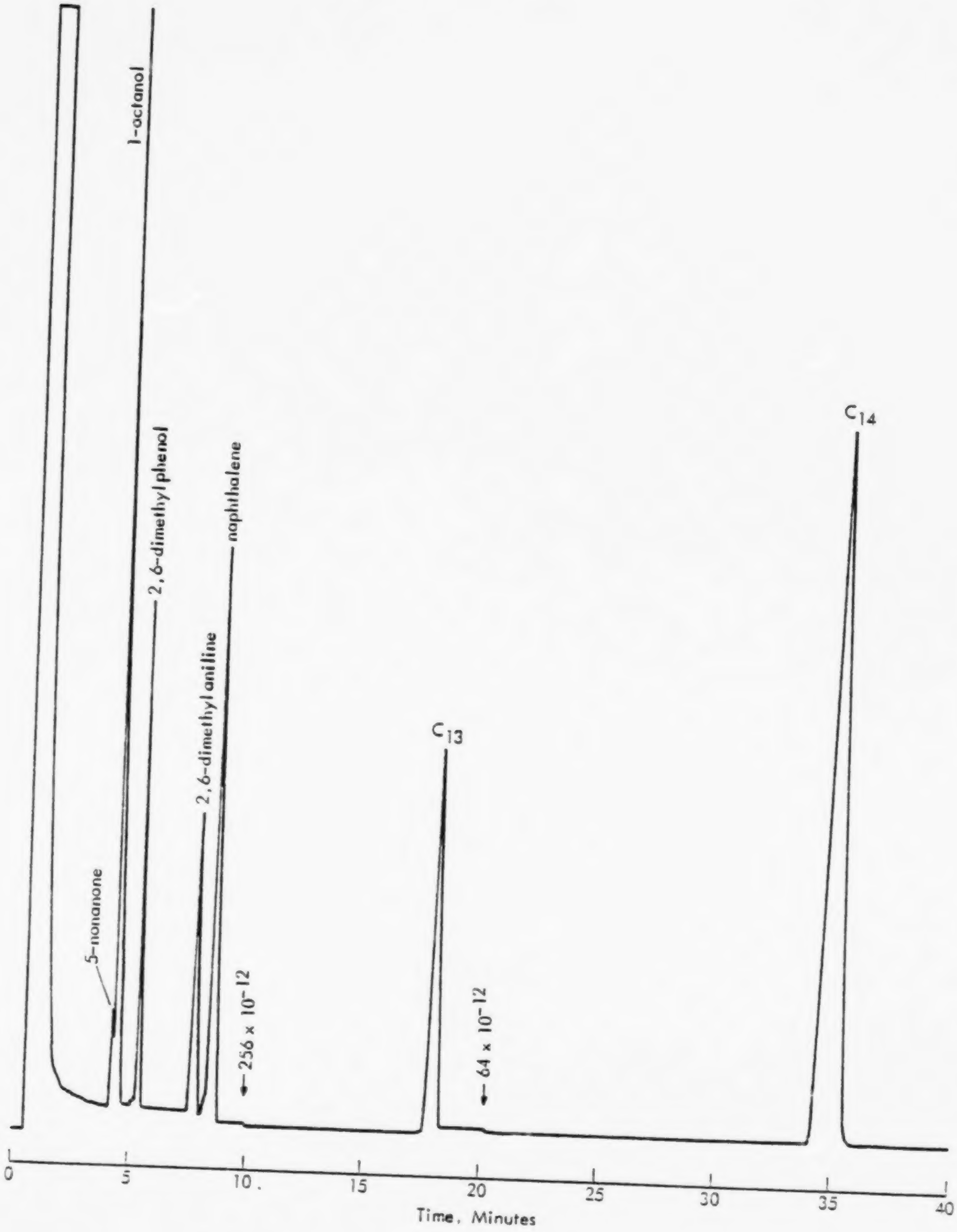

Figure 39. HRGC/FID chromatogram of a performance test solution on the fused silica SE-54 capillary column eluted with nitrogen.

TABLE 47. RESULTS OF THE WCOT CAPILLARY COLUMN EVALUATIONS

Column type	Carrier gas	Compound selected for HETP (determined)	HETP (mm)	Asymmetry (AS)			Adsorption			
				1-Octanol	Naphthalene	Octanone	1-Octanol/C_{12}[a]	DMA/C_{12}[b]	DMP/C_{12}[c]	pH[d]
SP-2100	Nitrogen	C_{13}	1.45	e	120	300	0.3	0.99	1.02	0.97
SP-2100 (Carbowax 20M)	Nitrogen	C_{16}	0.48	220	100	92	0.1	1.12	1.08	1.12
SE-52	Nitrogen	C_{13}	0.6	150	210	100	0.8	0.75	1.58	0.47
SE-54	Nitrogen	C_{13}	0.36	100	110	e	-	0.84	1.33	0.63
	Hydrogen	C_{13}	0.25	100	130	e	0.80[f]	0.71	1.16	0.62

[a] Ratio of peak heights, 1-octanol/C_{12}.

[b] Ratio of peak heights, 2,4-dimethylaniline/C_{12}.

[c] Ratio of peak heights, 2,6-dimethylphenol/C_{12}.

[d] Ratio of peak heights, 2,4-dimethylaniline/2,6-dimethylphenol.

[e] Asymmetry not determined. Octanone was not present in the test mixture used.

[f] Ratio of peak heights, 1-octanol/C_{10}.

Peak asymmetry (AS), a measure of the adsorption activity, was calculated for selected compounds from the formula:

$$AS = \frac{W_B}{W_F} \times 100$$

where W_B and W_F are the back and front baseline widths of the peak measured from a line bisecting the peak maximum. AS values were calculated for 1-octanol, naphthalene, and octanone. A more reliable indication of a column's activity for adsorption is the ratio of peak heights for a compound susceptible to adsorption and an inert compound. These adsorption ratios were calculated for 1-octanol, 2,4-dimethylaniline, and 2,6-dimethylphenol versus dodecane. The aniline and phenol adsorption values, as well as the pH of the column (the ratio of peak heights for the aniline and phenol), provide an indication of the acidic or basic character of the columns.

Of the four columns tested, the SE-54 fused silica column exhibited the best overall performance. The HETPs for the SE-54 column indicate much higher resolving power. The asymmetry and adsorption parameters indicate that the column, although slightly acidic, is fairly inert. The influence of the carrier gas on the performance of the SE-54 fused silica column was only apparent in the lower HETPs observed with hydrogen. Helium, typically used for GC/MS should provide similar performance with HETPs between those observed for nitrogen and hydrogen.

The absolute and relative retention times and response factors for the extractable spiking compounds are listed in Tables 48 and 49. All relative retention times and response factors were calculated using the d_{10}-anthracene internal standard for reference. The shorter retention times observed for compounds chromatographed on the SE-52 and SE-54 columns with hydrogen as the carrier gas reflect the higher linear velocity needed to achieve maximum efficiency. The use of hydrogen significantly shortened the total analysis time over nitrogen elution with no sacrifice in resolution. The chromatography observed was generally satisfactory for all compounds on all columns except that two pairs of compounds, 3,3'dichlorobenzidine and bis(2-ethylhexyl)phthalate and pentachlorophenol and d_{10}-anthracene, were not separated on the SE-52 column. The latter pair was also not separated on the SE-54 column. However, the best chromatography for benzidine was observed on the SE-54 column.

Although good chromatography was observed for the acidic compounds in standard solutions on all column systems, the phenols are likely to be very susceptible to adsorption on a partially active column. Analysis of acidic sludge extracts, cleaned by GPC only, would likely increase the adsorption character of capillary columns. In addition, the extracts for many sludges contain high levels of aliphatic hydrocarbons not removed by GPC which can hinder GC/MS analysis. Hence, capillary GC/MS may not be practicable for routine analyses of acidic sludge extracts.

TABLE 48. RELATIVE RETENTION TIMES AND RELATIVE RESPONSE FACTORS DETERMINED FOR THE BASE/NEUTRAL SPIKING COMPOUNDS BY CAPILLARY GC/FID

Compound	SP-2100				Fused silica SP-2100 (Carbowax 20M deactivated)			
	RT (min)	RRT	RF (mm/ng)	RRF	RT (min)	RRT	RF (mm/ng)	RRF
1,4-Dichlorobenzene	14.57	0.35	0.63	0.60	8.56	0.26	1.42	2.37
Hexachloroethane	17.52	0.42	0.27	0.26	10.63	0.32	0.33	0.55
Bis(2-chloroisopropyl)ether	16.54	0.39	0.63	0.60	9.84	0.30	0.64	1.07
Bis(2-chloroethyl)ether	13.19	0.31	0.26	0.25	7.78	0.24	0.97	1.62
Acenaphthylene	31.50	0.75	1.89	2.80	23.03	0.70	1.60	2.67
2,6-Dinitrotoluene	30.91	0.74	0.41	0.39	23.52	0.71	0.24	0.40
Fluoranthene	49.21	1.17	0.46	0.44	39.96	1.21	0.26	0.43
Benzidine	51.38	1.23	0.007	0.007	ND[a]	-	ND	-
3,3'-Dichlorobenzidine	59.45	1.42	0.003	0.003	46.46	1.41	0.12	0.20
n-Butylbenzylphthalate	55.73	1.33	0.30	0.29	45.87	1.39	0.23	0.38
Bis(2-ethylhexyl)phthalate	60.24	1.44	0.56	0.53	51.08	1.55	0.06	0.10
Benzo[*a*]pyrene	67.13	1.60	0.02	0.02	57.28	1.74	0.003	0.005
d_{10}-Anthracene	41.93	1.00	1.05	1.00	32.97	1.00	0.60	1.00

Compound	SE-52 (N_2)				SE-52 (H_2)			
	RT (min)	RRT	RF (mm/ng)	RRF	RT (min)	RRT	RF (mm/ng)	RRF
1,4-Dichlorobenzene	9.06	0.26	1.49	1.52	9.55	0.45	2.53	3.24
Hexachloroethane	11.02	0.32	0.29	0.30	10.83	0.50	1.43	1.83
Bis(2-chloroisopropyl)ether	10.43	0.30	0.59	0.60	10.63	0.49	1.05	1.35
Bis(2-chloroethyl)ether	8.46	0.25	1.02	1.04	9.25	0.43	2.34	3.00
Acenaphthylene	24.21	0.70	0.94	0.96	17.13	0.80	3.81	4.88
2,6-Dinitrotoluene	25.39	0.74	0.04	0.04	17.72	0.83	0.32	0.41
Fluoranthene	41.54	1.21	0.03	0.03	24.41	1.14	0.65	0.83
Benzidine	44.29	1.29	0.02	0.02	ND	-	-	-
3,3'-Dichlorobenzidine	51.57	1.50	0.05	0.05	28.54	1.33	b	-
n-Butylbenzylphthalate	48.43	1.41	0.07	0.07	26.97	1.26	0.58	0.74
Bis(2-ethylhexyl)phthalate	52.36	1.52	0.08	0.08	28.54	1.33	b	-
Benzo[*a*]pyrene	59.06	1.71	0.03	0.03	31.79	1.48	0.10	0.13
d_{10}-Anthracene	34.45	1.00	0.98	1.00	21.46	1.00	0.78	1.00

Compound	SE-54 (N_2)				SE-54 (H_2)			
	RT (min)	RRT	RF (mm/ng)	RRF	RT (min)	RRT	RF (mm/ng)	RRF
1,4-Dichlorobenzene	9.25	0.26	2.85	13.57	3.15	0.12	4.50	8.04
Hexachloroethane	11.81	0.33	0.60	2.86	4.72	0.18	0.63	1.13
Bis(2-chloroisopropyl)ether	11.22	0.31	0.66	3.14	4.53	0.17	0.92	1.64
Bis(2-chloroethyl)ether	8.66	0.24	1.77	8.43	2.76	0.10	3.33	5.95
Acenaphthylene	25.39	0.71	0.92	4.38	17.32	0.65	1.51	2.70
2,6-Dinitrotoluene	26.57	0.74	0.05	0.24	18.50	0.70	0.34	1.62
Fluoranthene	42.72	1.19	0.20	0.95	33.27	1.25	0.27	0.48
Benzidine	44.49	1.24	0.02	0.10	35.43	1.33	0.03	0.14
3,3'-Dichlorobenzidine	52.36	1.46	0.02	0.10	42.32	1.59	0.06	0.29
n-Butylbenzylphthalate	49.61	1.38	0.15	0.71	40.35	1.52	0.33	0.59
Bis(2-ethylhexyl)phthalate	53.74	1.50	0.12	0.57	44.69	1.68	0.22	0.39
Benzo[*a*]pyrene	59.65	1.66	0.05	0.24	48.62	1.83	0.05	0.09
d_{10}-Anthracene	35.83	1.00	0.21	1.00	26.57	1.00	0.56	1.00

[a] ND = not detected.

[b] Response factors were not determined for 3,3'-dichlorobenzidine and bis(2-ethylhexyl)phthalate because they coeluted.

TABLE 49. RELATIVE RETENTION TIMES AND RELATIVE RESPONSE FACTORS DETERMINED FOR THE ACIDIC SPIKING COMPOUNDS BY CAPILLARY GC/FID

	SP-2100				Fused silica SP-2100 (Carbowax 20M deactivated)			
Compound	RT (min)	RRT	RF (mm/ng)	RRF	RT (min)	RRT	RF (mm/ng)	RRF
Phenol	9.06	0.37	0.44	0.85	11.22	0.34	0.81	0.79
2,4-Dimethylphenol	12.80	0.53	0.12	0.23	15.35	0.47	0.76	0.75
2,4-Dichlorophenol	13.39	0.55	0.09	0.17	16.54	0.50	0.24	0.24
Pentachlorophenol	23.82	0.98	0.09	0.17	34.84	1.06	0.02	0.02
D_{10}-Anthracene	24.21	1.00	0.52	1.00	32.87	1.00	1.02	1.00

	SE-52 (N_2)			
Compound	RT (min)	RRT	RF (mm/ng)	RRF
Phenol	8.66	0.44	0.86	0.88
2,4-Dimethylphenol	11.02	0.56	1.06	1.08
2,4-Dichlorophenol	11.61	0.59	0.17	0.17
Pentachlorophenol	19.69	1.00	0.07	0.07
D_{10}-Anthracene	19.69	1.00	0.98	1.00

	SE-54 (N_2)				SE-54 (H_2)			
Compound	RT (min)	RRT	RF (mm/ng)	RRF	RT (min)	RRT	RF (mm/ng)	RRF
Phenol	4.53	0.24	3.31	5.34	2.17	0.14	5.16	15.18
2,4-Dimethylphenol	7.68	0.41	2.11	3.40	4.92	0.32	0.90	2.65
2,4-Dichlorophenol	8.27	0.44	1.07	1.76	5.31	0.35	0.62	1.82
Pentachlorophenol	18.5	0.99	ND[a]	-	15.34	1.00	0.12	0.35
D_{10}-Anthracene	18.7	1.00	0.62	1.00	15.35	1.00	0.34	1.00

[a] ND = not detected.

Evaluation of the SE-54 Fused Silica Column for Analyses of Sludge Extracts--

The suitability of the SE-54 fused silica column for analyses of sludge extracts was evaluated by chromatographing the spiked sludge extracts prepared for the evaluation of adsorption chromatographic cleanup procedures. In addition, retention time and response factor data were generated for the entire list of B/N priority pollutants.

Experimental--Extracts that were prepared from 80-ml aliquots of sludge, spiked with the B/N spiking compounds, and then cleaned with florisil or silica gel were analyzed by GC/MS using the 15-m SE-54 WCOT capillary column eluted with helium.

Solutions of the B/N priority pollutant compounds at various concentrations were analyzed with the same capillary GC/MS system, and retention times and response factors were compiled.

Results and discussion--The capillary GC/MS, or high resolution GC/MS (HRGC/MS), chromatograms for composited and individual fractions from silica gel cleanup of spike sludge extracts are shown in Figures 40 to 43. Comparison of these chromatograms with the packed column GC/MS chromatograms for similar fractions from florisil cleanup (Figures 31 to 34) illustrate the much better chromatographic resolution provided by the capillary column. Interpretation of the HRGC/MS data was made considerably easier by the separations achieved.

The relative retention time data generated for the B/N compounds are shown in Table 50. Table 51 shows the relative response factors determined for many of the B/N priority pollutants. The relative response factors for most of the compounds, except benzidine and 2,6-dinitrotoluene, were fairly consistent over the range of 4 to 200 ng injected. Nonetheless, these data confirm the principle that the response for a particular compound should be checked over the entire range of concentrations quantitated.

SELECTION OF METHODS FOR EXTRACTABLE COMPOUNDS IN MUNICIPAL AND INDUSTRIAL WASTEWATER TREATMENT SLUDGE

Although the methods described in the preliminary POTW sludge protocol for analyzing base/neutral and acidic compounds provided acceptable precision and accuracy for most compounds, some shortcomings were apparent. Homogenization/centrifugation extraction of 320-ml aliquots of sludge was both labor-intensive and time-consuming. The rigorous extraction also produced an extract enriched in interfering coextractants which challenged the capacity of the GPC cleanup. Unfortunately, none of the alternate extraction procedures was found to provide recoveries for the broad range of the basic, neutral, and acidic compounds that were comparable to those demonstrated for homogenization/centrifugation. Hence, the homogenization/centrifugation extraction was recommended for analyses of both municipal and industrial sludge with one modification. Extraction of a single 80-ml aliquot of sludge was recommended to decrease the time required for extract preparation. Since extracts from 80-ml aliquots were analyzed at a smaller final volume, there was no real decrease in method sensitivity.

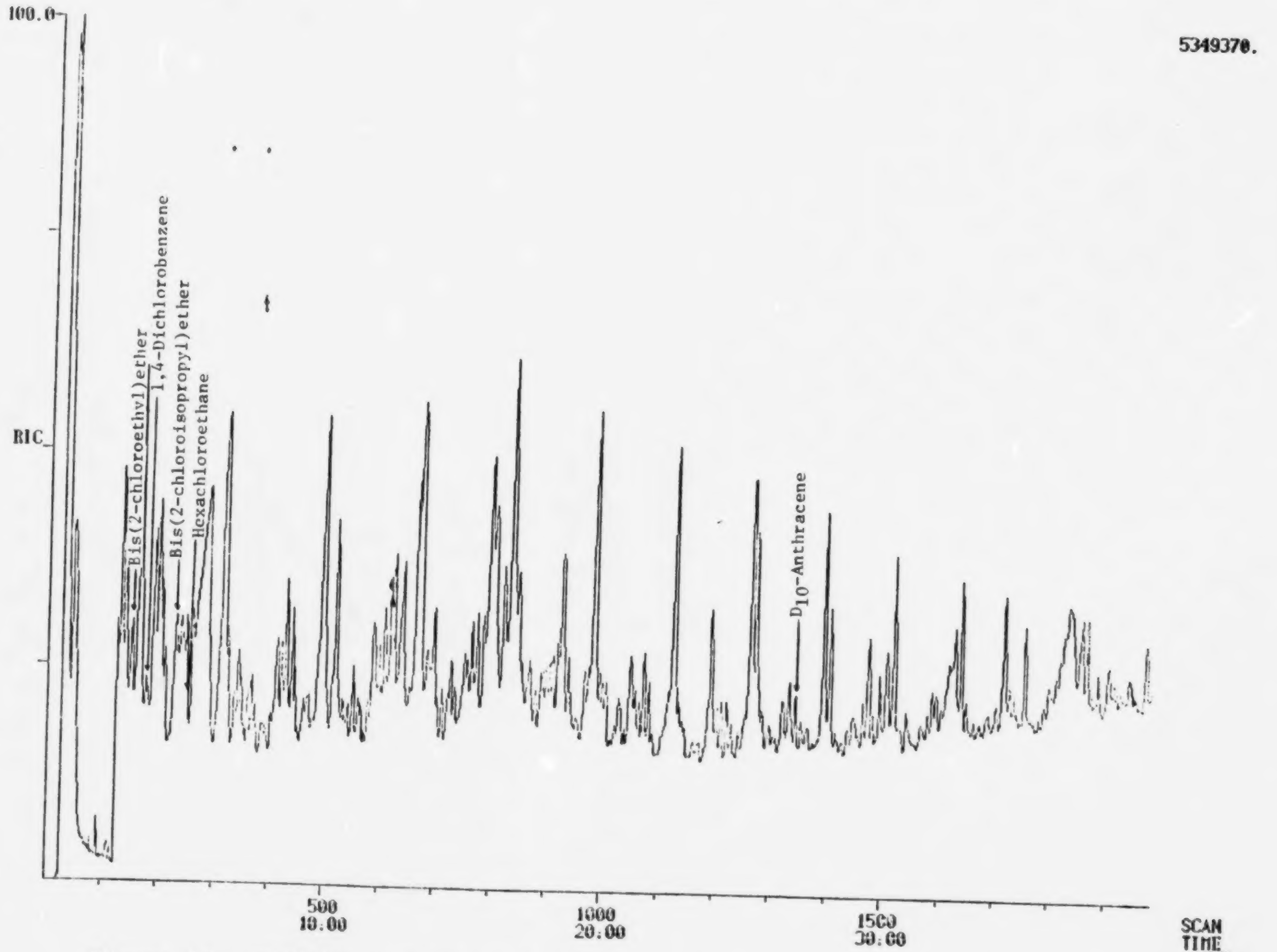

Figure 40. HRGC/MS chromatogram of the combined eluent (Fractions II-IV) obtained by silica gel cleanup of the spiked sludge extract (no GPC cleanup).

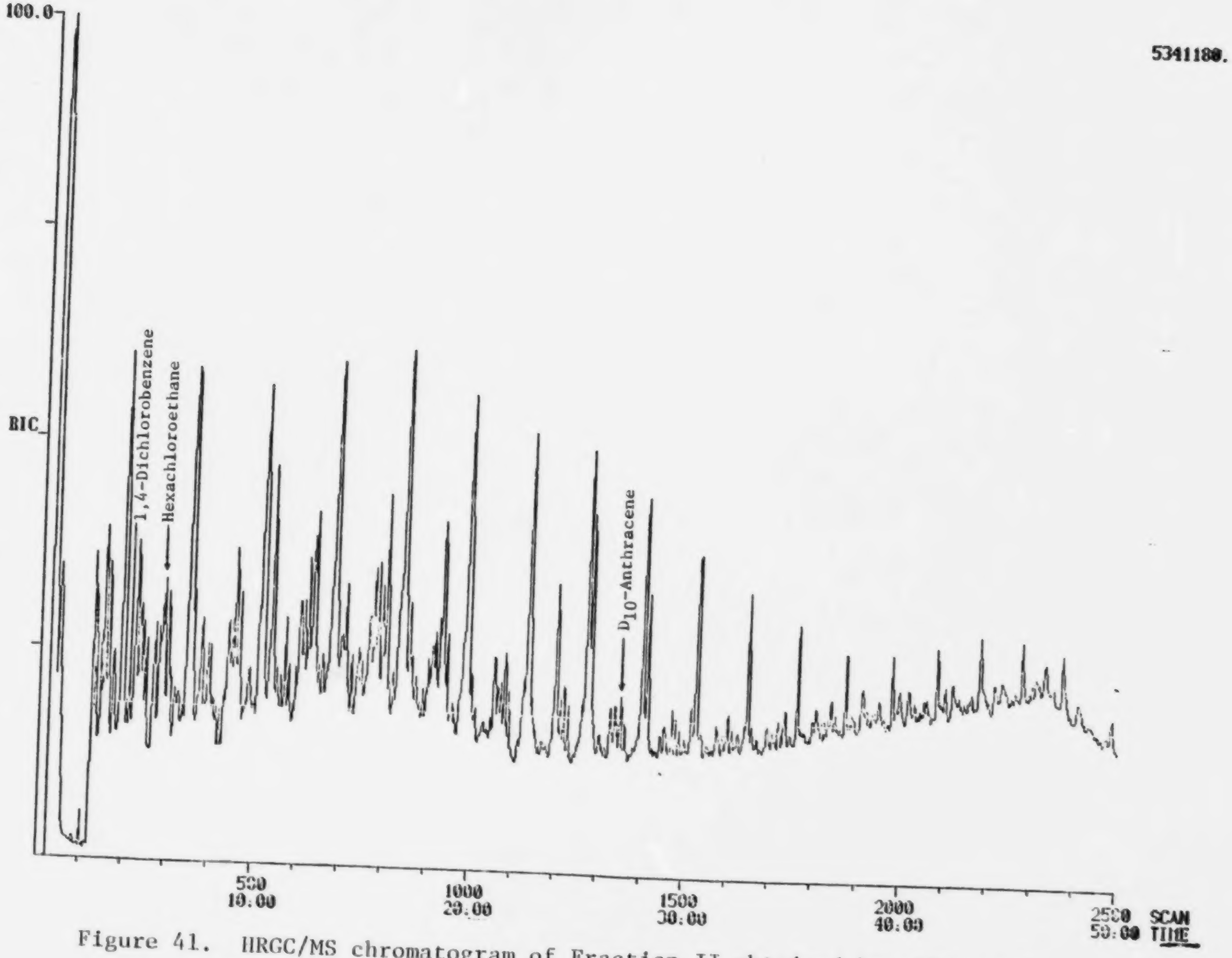

Figure 41. HRGC/MS chromatogram of Fraction II obtained by silica gel cleanup of the spiked sludge extract (no GPC cleanup).

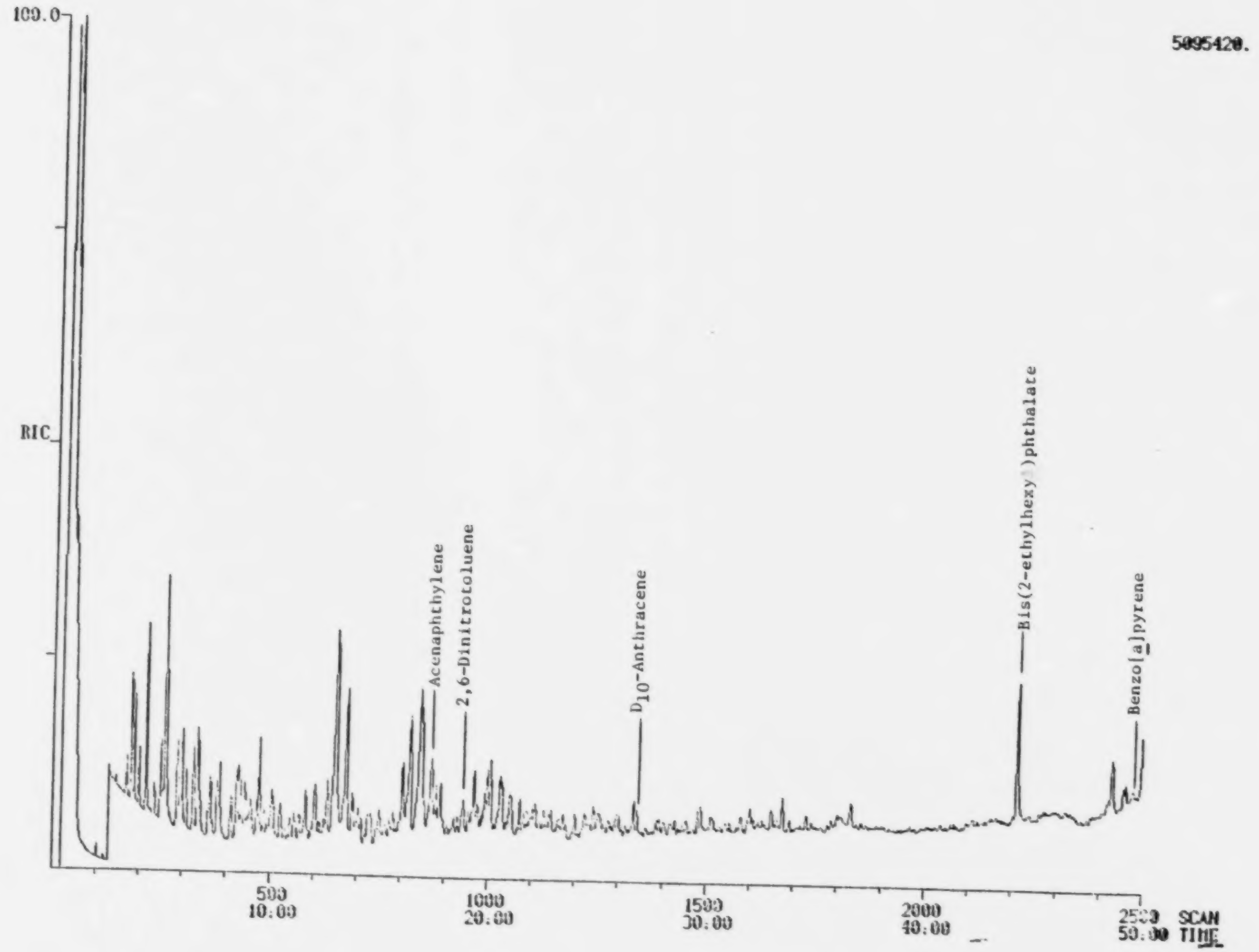

Figure 42. HRGC/MS chromatogram of Fraction III obtained by silica gel cleanup of the spiked sludge extract (no GPC cleanup).

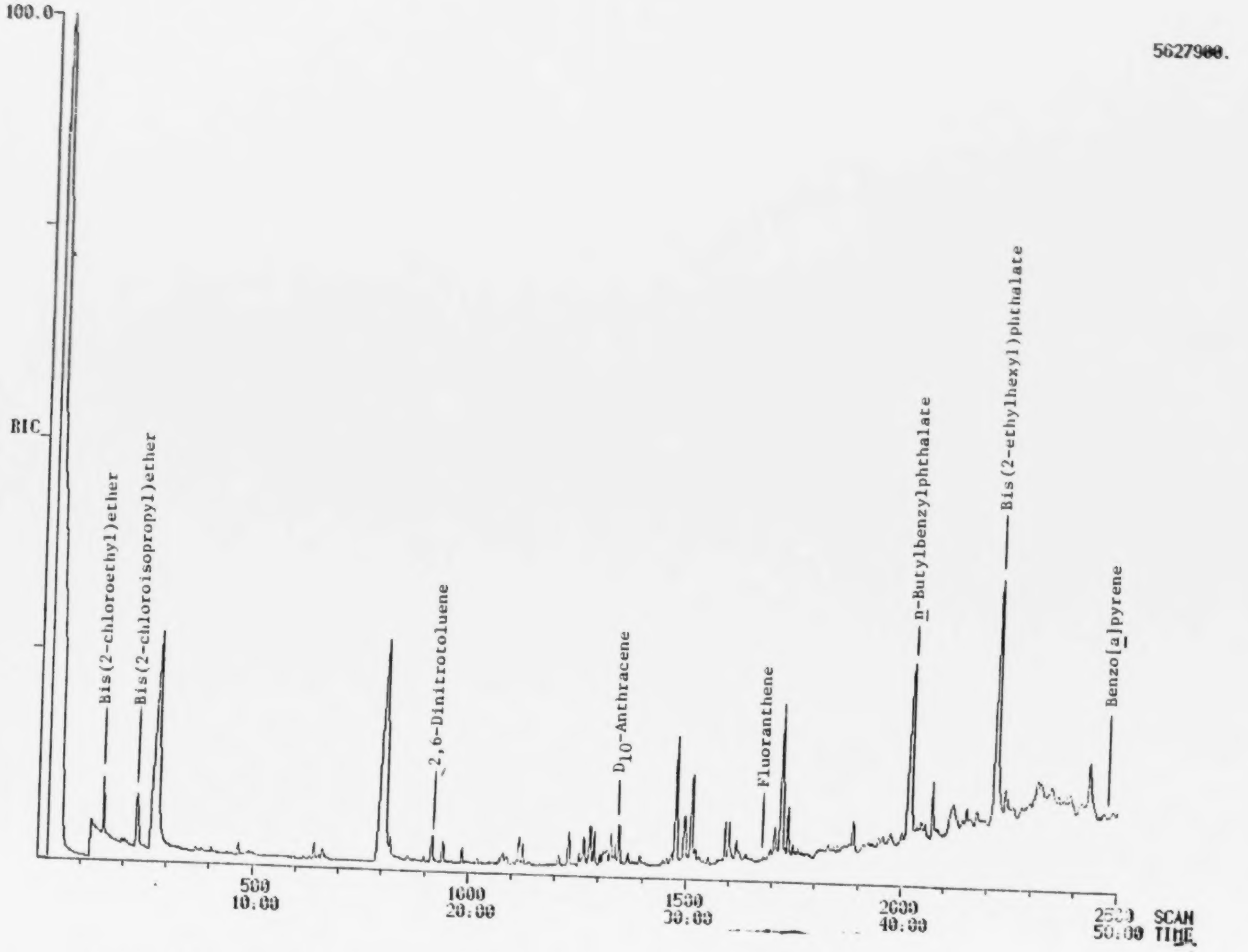

Figure 43. HRGC/MS chromatogram of Fraction IV obtained by silica gel cleanup of the spiked sludge extract (no GPC cleanup).

TABLE 50. RELATIVE RETENTION TIMES FOR THE BASE/NEUTRAL COMPOUNDS ANALYZED BY CAPILLARY COLUMN GC/MS

Compound name	RRT[a]
N-nitrosodimethylamine	0.04
Bis(2-chloroethyl)ether	0.21
1,3-Dichlorobenzene	0.22
1,4-Dichlorobenzene	0.22
1,2-Dichlorobenzene	0.25
Bis(2-chloroisopropyl)ether	0.29
Hexachloroethane	0.29
N-Nitrosodi-n-propylamine	0.31
Nitrobenzene	0.32
Isophorone	0.36
Bis(2-chloroethoxy)methane	0.41
1,2,4-Trichlorobenzene	0.42
Naphthalene	0.43
Hexachlorobutadiene	0.47
Hexachlorocyclopentadiene	0.60
2-Chloronaphthalene	0.63
Acenaphthylene	0.70
Dimethylphthalate	0.72
2,6-Dinitrotoluene	0.72
Acenaphthene	0.73
2,4-Dinitrotoluene	0.78
Fluorene	0.82
4-Chlorophenylphenylether	0.84
Diethylphthalate	0.84
N-Nitrosodiphenylamine[b]	0.84
1,2-Diphenylhydrazine[c]	0.86
4-Bromophenylphenylether	0.92
Hexachlorobenzene	0.93
Phenanthrene	0.98
Anthracene	0.99
D_{10}-Anthracene	1.00
Di-n-butylphthalate	1.14
Fluoranthene	1.19
Pyrene	1.23
Benzidine	1.24
Butylbenzylphthalate	1.40
Chrysene	1.45
3,3'-Dichlorobenzidine	1.47
Bis(2-ethylhexyl)phthalate	1.52
Benzo[*k*]fluoranthene	1.62
Di-n-octylphthalate	1.63
Benzo[*a*]pyrene	1.67
Dibenzo[*a*,*h*]anthracene	1.84
Benzo[g,*h*,*i*]perylene	1.87

[a] RRT = relative retention time based on D_{10}anthracene (RRT = 1.00) for compounds chromatographed on a SE-54 WCOT fused silica capillary (15 m x 0.24 mm ID) eluted with helium at 10 psi and with a temperature program of 50°C for 4 min, then 4°C/min to 320°C.

[b] Elutes a diphenylamine.

[c] Elutes as azobenzene.

TABLE 51. GC/MS RELATIVE RESPONSE FACTORS FOR THE BASE/NEUTRAL PRIORITY POLLUTANTS

Compound	Ion used for quantitation (m/e)	Relative response factor[a]					
		Amount injected					
		4 ng	20 ng	40 ng	80 ng	100 ng	200 ng
1,2-Dichlorobenzene	146	NA[b]	NA	1.26	1.31	NA	NA
1,3-Dichlorobenzene	146	NA	NA	1.10	1.33	NA	NA
1,4-Dichlorobenzene	146	0.38	0.52	NA	NA	0.39	0.46
Hexachloroethane	117	0.25	0.30	NA	NA	0.22	0.25
Bis(2-chloroisopropyl)ether	45	NA	NA	NA	NA	NA	NA
Bis(2-chloroethyl)ether	93	0.42	0.59	NA	NA	0.57	0.54
Nitrobenzene	77	NA	NA	3.72	1.26	NA	NA
Hexachlorobutadiene	225	NA	NA	0.42	0.47	NA	NA
Naphthalene	128	NA	NA	3.32	2.59	NA	NA
2-Chloronaphthalene	162	NA	NA	1.54	1.38	NA	NA
Acenaphthylene	152	1.73	1.76	NA	NA	1.26	0.55
Acenaphthene	154	NA	NA	1.24	1.28	NA	NA
2,6-Dinitrotoluene	165	0.13	0.23	NA	0.40	0.21	0.17
Fluorene	166	NA	NA	1.11	1.31	NA	NA
4-Bromophenylphenylether	248	NA	NA	0.31	0.31	NA	NA
Fluoranthene	202	0.88	0.86	1.08	1.18	0.81	0.47
Pyrene	202	NA	NA	1.08	1.11	NA	NA
Benzidine	184	0.04	0.11	NA	NA	0.22	0.15
3,3'-Dichlorobenzidine	252	NA	NA	NA	NA	NA	NA
n-Butylbenzylphthalate	149	0.55	0.55	NA	NA	0.61	0.44
Bis(2-ethylhexyl)phthalate	149	0.94	0.98	NA	NA	0.93	0.47
Benzo[a]pyrene	252	0.24	0.25	NA	NA	0.28	0.21
d_{10}-Anthracene	188	1.00	1.00	1.00	1.00	1.00	1.00

a Relative to d_{10}-anthracene.

b NA = not analyzed.

Both GPC and adsorption chromatography on florisil and silica gel provided acceptable extract cleanup and recoveries for the B/N compounds. The florisil and silica gel adsorbent methods were essentially equivalent. The florisil and silica gel methods removed aliphatic hydrocarbons and low and high molecular weight polar interferences. Although the GPC method only removes mostly high molecular weight biogenic materials, it is easier to automate and is more amenable to routine sludge analyses. GPC was the only cleanup procedure that provided good recoveries for the acidic compounds. Hence, GPC and adsorption chromatography on florisil or silica gel were recommended as options for cleaning B/N extracts. GPC was recommended for cleanup of acidic extracts.

Although the packed column GC/MS method described in the preliminary POTW protocol provided reliable analyses of sludge extracts, the SE-54 WCOT fused silica capillary column was recommended as the preferred option for the GC/MS procedure for B/N extracts. The better resolution and inertness of the SE-54 capillary column provided GC/MS data that were easier to interpret. However, the HRGC/MS method should only be used for extracts cleaned by chromatography on florisil or silica gel. The packed column GC/MS method was recommended for analyses of acidic extracts. The level of cleanup provided by the GPC cleanup for acidic extracts may make it difficult to maintain the inactivity of the capillary column.

The revised analytical scheme for extractable priority pollutants in municipal and industrial wastewater treatment sludges is shown in Figure 44. The detailed analytical protocol prepared from this scheme is appended to this report.

EVALUATION OF THE PRECISION AND ACCURACY OF THE METHOD

The precision and accuracy of the extractables protocol (Appendix B) were evaluated by determining recoveries of the spiked compounds from five primary sludges. The sludges used in these evaluations were those described in Table 18. Recoveries were determined for the extractable compounds fortified into aliquots of these sludges at three spiking levels. The spiking levels were chosen to be 2, 20, and 200 times the individual detection limit typically observed for each compound in sludge. Two combinations of cleanup-analysis options were evaluated for the B/N compounds. B/N extracts were analyzed by packed column GC/MS following GPC cleanup and by capillary GC/MS following florisil cleanup. All acidic sludge extracts were cleaned up by GPC and analyzed by packed column GC/MS.

Experimental

Eleven 80-ml aliquots of each of the five primary sludge samples were placed in 200-ml centrifuge bottles fitted with TFE-lined septa. Three sets of triplicate bottles were spiked with the extractable spiking compounds at 400, 4,000 and 40,000 μg/liter sludge. Benzidine was spiked at 800, 8,000, and 80,000 μg/liter sludge. The spikes were added in 2 to 3 ml of acetone solution. Immediately following the addition of the spikes, samples were homogenized for 30 to 45 s and stored at 4°C overnight prior to analysis. The unspiked sludges were analyzed in duplicate and the spiked sludges were analyzed in triplicate by the procedures described in Method Appendix.

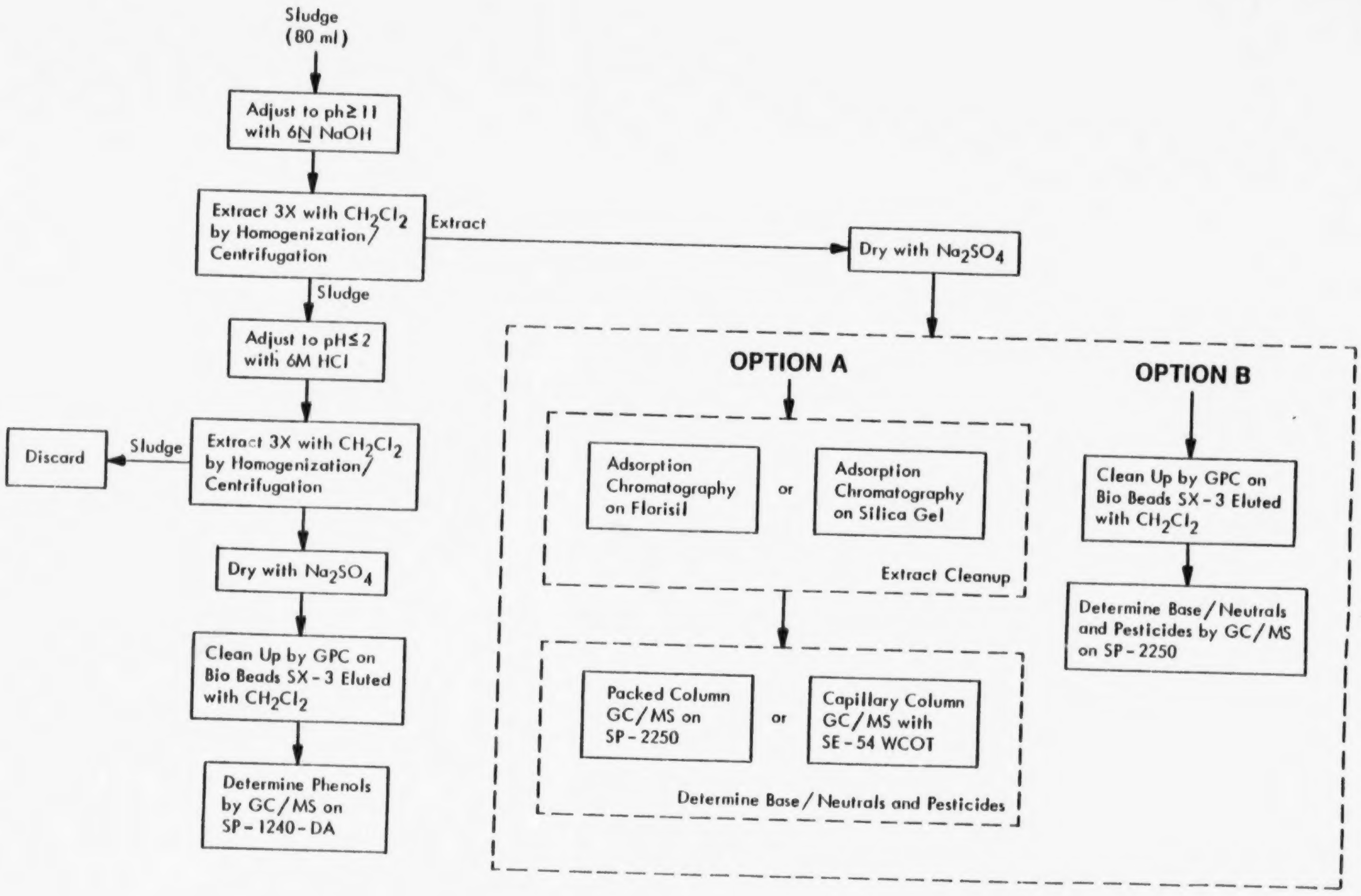
Sludge
(80 ml)
Adjust to ph≥11 with 6N NaOH
Extract 3X with CH2Cl2 by Homogenization/ Centrifugation
Extract
Dry with Na2SO4
Sludge
Adjust to pH≤2 with 6M HCl
Extract 3X with CH2Cl2 by Homogenization/ Centrifugation
Sludge
Discard
Dry with Na2SO4
Clean Up by GPC on Bio Beads SX-3 Eluted with CH2Cl2
Determine Phenols by GC/MS on SP-1240-DA
OPTION A
Adsorption Chromatography on Florisil
or
Adsorption Chromatography on Silica Gel
Extract Cleanup
Packed Column GC/MS on SP-2250
or
Capillary Column GC/MS with SE-54 WCOT
Determine Base/Neutrals and Pesticides
OPTION B
Clean Up by GPC on Bio Beads SX-3 Eluted with CH2Cl2
Determine Base/Neutrals and Pesticides by GC/MS on SP-2250

Figure 44. Scheme for analysis of extractable organics in sludge.

Results and Discussion

The results of the precision and accuracy determinations for the B/N compounds obtained with GPC cleanup and packed column GC/MS are shown in Table 52. The GC/MS chromatograms shown in Figures 45 to 52 are representative samples of the data generated. Figures 45 to 48 are chromatograms for unspiked and spiked aliquots of Platte County POTW sludge. Chromatograms for unspiked aliquots of sludges from the remaining four plants are shown in Figures 49 to 52. Many of the recovery determinations were likely perturbated by high concentrations of the analytes in the unspiked sludge samples. Recoveries were not calculated for cases where the unspiked concentration was greater than 10 times the spike level. Although the recoveries varied somewhat from sludge to sludge for many compounds, all compounds were recovered from all five sludges spiked at 40,000 μg/liter. Recoveries were generally lower for the polar compounds, including 2,6-dinitrotoluene, the benzidines, and bis-(2-chloroethyl)ether. However, only 2,6-dinitrotoluene was not recovered from all sludges spiked at 400 μg/liter. Of all recovery determinations, 49% fell within the range of 50 to 150%. An additional 19% were lower than 50% recovery, and only 8% of the recoveries were greater than 150%.

The accuracy of the method was somewhat dependent on the particular sludge samples. However, the precisions of the recovery determinations were very good. The relative standard deviations for triplicate determinations were 30% or less for 95% of the measurements and 10% or less for 62% of the measurements.

The recoveries for B/N compounds from spiked sludge obtained with florisil cleanup and capillary GC/MS are shown in Table 53. Figures 53 to 60 show the HRGC/MS chromatograms for unspiked and spiked sludges from the Platte County POTW and for unspiked sludges from the other plants. Although these sludges are replicate samples of those spiked and analyzed with the packed column GC/MS method, the levels determined in the unspiked samples by the capillary column GC/MS method were lower. This likely reflects losses during sample storage as the samples were extracted for the capillary column GC/MS experiments 2 to 3 weeks later than for the packed column GC/MS study. In general, the recoveries were similar to those observed with the packed column GC/MS option. However, all compounds were recovered from all five sludges spiked at 400 μg/liter. An investigation of the distribution of the recoveries shows that 48% were within the range of 50 to 150%, 28% were less than 50%, and 13% were higher than 150% recovery. The reproducibility of the determinations was slightly poorer. Fifty-six percent of the relative standard deviation (RSD) values were 30% or less. Of these, 30% are less than 10% RSD. The poorer precision observed with the HRGC/MS method may reflect the influence of repeated injections of sludge extracts on the performance of the capillary column. Concentrated samples can overload the column and degrade the column performance. The reproducibility of HRGC/MS determinations for extracts from the high level spikes was better than for other extracts. Eighty-four percent of the extracts from samples spiked at 40,000 μg/liter had RSDs of less than 30%.

TABLE 52. RESULTS OF PRECISION AND ACCURACY EVALUATIONS FOR THE EXTRACTABLES METHOD (PACKED COLUMN GC/MS) APPLIED TO THE ANALYSIS OF BASE/NEUTRAL COMPOUNDS IN MUNICIPAL AND INDUSTRIAL WASTEWATER TREATMENT SLUDGES

		Platte County POWW			Blue River POTW			Kansas City, Ks			Industrial No. 1			Industrial No. 2	
Compound	Spike conc. (µg/L)	Unspiked[a] sludge (µg/L)	Recovery (%)	Spike conc. (µg/L)	Unspiked[a] conc. (µg/L)	Recovery (%)	Spike conc. (µg/L)	Unspiked[a] conc. (µg/L)	Recovery (%)	Spike conc. (µg/L)	Unspiked[a] conc. (µg/L)	Recovery (%)	Spike conc. (µg/L)	Unspiked[a] conc. (µg/L)	Recovery (%)
1,4-Dichlorobenzene	417	45	70 ± 9[b]	400	47	37 ± 21	400	21	11 ± 3	400	ND	51 ± 4	400	820	c
	4,160		87 ± 2	4,000		77 ± 7	4,000		93 ± 9	4,000		73 ± 5	4,000		88 ± 12
	41,610		74 ± 8	39,990		87 ± 7	39,990		90 ± 9	39,900		70 ± 4	40,000		92 ± 9
Hexachloroethane	441	ND[d]	39 ± 3	400	ND	0	400	ND	0	400	ND	17 ± 5	400	ND	0
	4,400		56 ± 7	4,000		54 ± 3	4,000		47 ± 8	4,000		55 ± 9	4,000		97 ± 6
	44,010		53 ± 2	40,000		59 ± 5	40,010		57 ± 10	39,990		51 ± 7	40,000		77 ± 4
Bis(2-chloroethyl)-ether	408	62	35 ± 5	400	ND	100 ± 54	400	ND	0	400	ND	88 ± 6	400	ND	0
	4,070		44 ± 2	4,000		380 ± 37	4,000		510 ± 123	4,000		120 ± 14	4,000		200 ± 4
	40,680		27 ± 4	39,990		280 ± 8	39,990		410 ± 53	40,000		95 ± 11	40,000		130 ± 7
Acenaphthylene	411	1	77 ± 6	400	1,430	43, 25[c]	400	ND	0	400	6	65 ± 3	400	ND	200 ± 34
	4,090		84 ± 7	4,000		42 ± 7	4,000		82 ± 12	4,000		89 ± 5	4,000		130 ± 52
	40,000		51 ± 2	39,900		41 ± 2	40,000		98 ± 10	39,000		88 ± 3	40,000		93 ± 2
2,6-Dinitrotoluene	407	ND	0	400	ND	0	400	ND	0	400	ND	0	400	ND	0
	4,050		0	4,000		20 ± 1	4,000		0	4,000		59 ± 8	4,000		150 ± 9
	40,550		63 ± 4	40,040		73 ± 3	40,040		78 ± 20	39,990		99 ± 14	40,000		97 ± 5
Fluoranthene	428	65	45 ± 5	400	8,330	e	400	124	16 ± 2	400	14	56 ± 8	400	670	c
	4,270		58 ± 5	4,000		59 ± 18	4,000		52 ± 14	4,000		82 ± 7	4,000		120 ± 1
	40,000		50 ± 4	39,530		20 ± 2	40,000		100 ± 6	39,920		100 ± 14	40,000		95 ± 4
Benzidine	789	ND	0	800	ND	0	800	ND	0	800	ND	38 ± 8	800	ND	0
	4,870		20 ± 1	8,000		0	8,000		0	8,000		82 ± 10	8,000		120 ± 7
	80,000		90 ± 7	79,080		96 ± 12	80,000		160 ± 13	80,000		130 ± 6	70,000		50 ± 2
3,3'-Dichlorobenzidine	415	ND	46 ± 6	402	ND	0	402	535	c	400	ND	0	NA	ND	-
	4,130		37 ± 2	4,020		100 ± 14	4,020		110 ± 13	4,000		0	NA		-
	NA		-	NA		-	NA		-	NA		-	NA		-
n-Butylbenzylphthalate	452	544	c	400	3,090	c	400	5,950	e	400	ND	57 ± 8	400	12,500	e
	4,500		20 ± 1	4,000		150 ± 17	4,000		210 ± 136[c]	4,000		54 ± 5	4,000		c
	40,000		59 ± 2	40,000		31 ± 2	40,000		300 ± 30	40,000		85 ± 7	40,000		80 ± 4
Bis(2-ethylbenzyl)-phthalate	444	652	c	400	2,850	c	400	1,790	c	400	85	30 ± 3	400	24,200	c
	4,430		22 ± 1	4,000		120 ± 5	4,000		190 ± 80	4,000		42 ± 4	4,000		230 ± 4[c]
	40,000		47 ± 3	40,000		28 ± 3	40,010		180 ± 21	40,000		53 ± 9	48,820		200 ± 10
Benzo[a]pyrene	NA[f]	ND	-	400	4,050	e	400	ND	0	400	ND	30 ± 1	400	308	0
	NA		-	4,000		290 ± 63[c]	4,000		80 ± 8	4,000		33 ± 4	4,000		140 ± 7
	40,550		56 ± 3	40,010		68 ± 10	40,010		140 ± 19	40,080		48 ± 4	40,000		97 ± 6

[a] Mean of two determinations.

[b] Mean ± standard deviation for three determinations.

[c] Concentration determined in the unspiked sludge was higher than the spike level.

[d] ND = not detected.

[e] Concentration determined in the unspiked sludge was 10 times higher than the spike level.

[f] NA = this compound was not available when these samples were spiked.

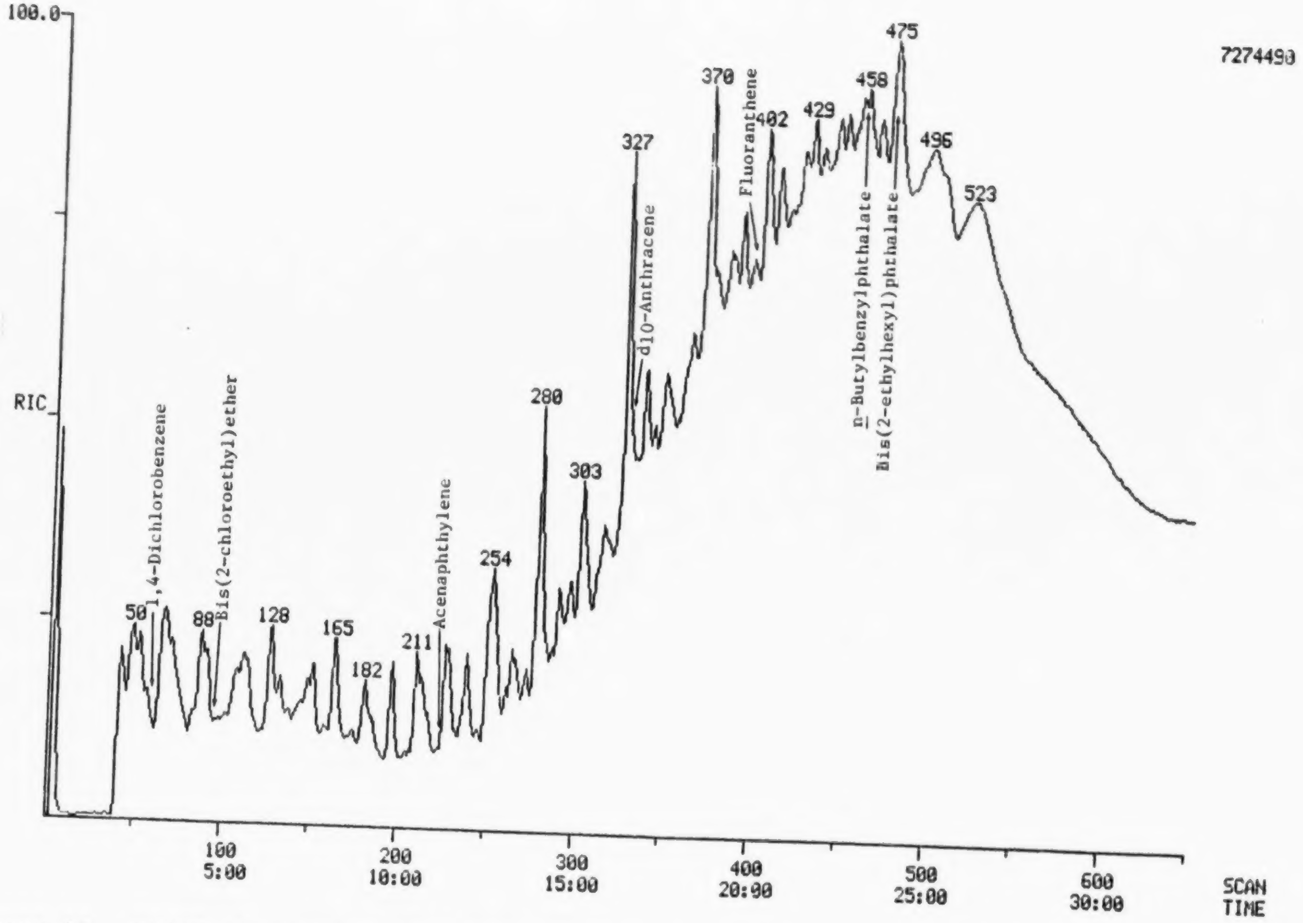

Figure 45. GC/MS chromatogram for base/neutrals in unspiked Platte County primary POTW sludge.

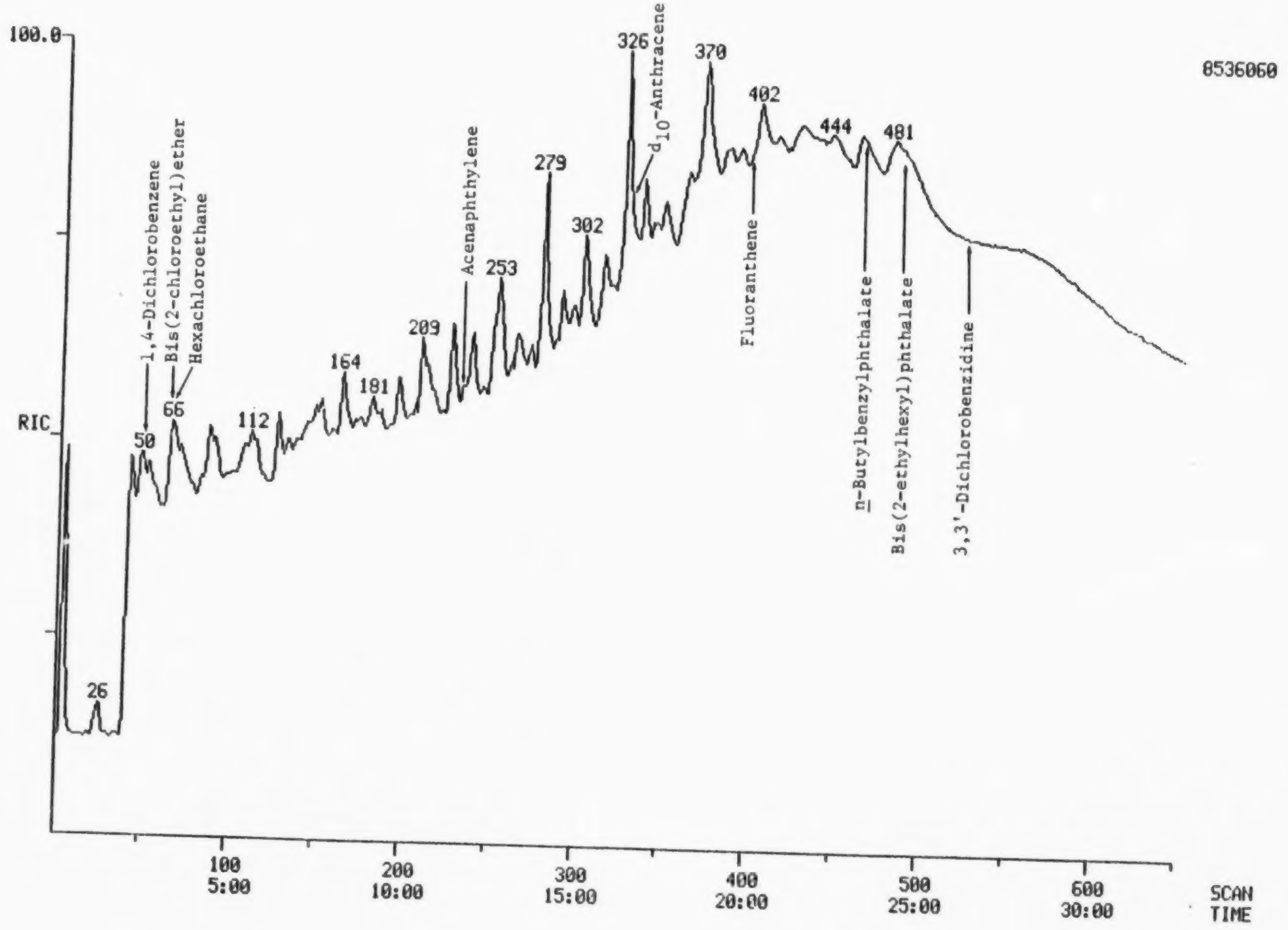

Figure 46. GC/MS chromatogram for base/neutrals in Platte County primary POTW sludge spiked at 400 μg/L with selected compounds.

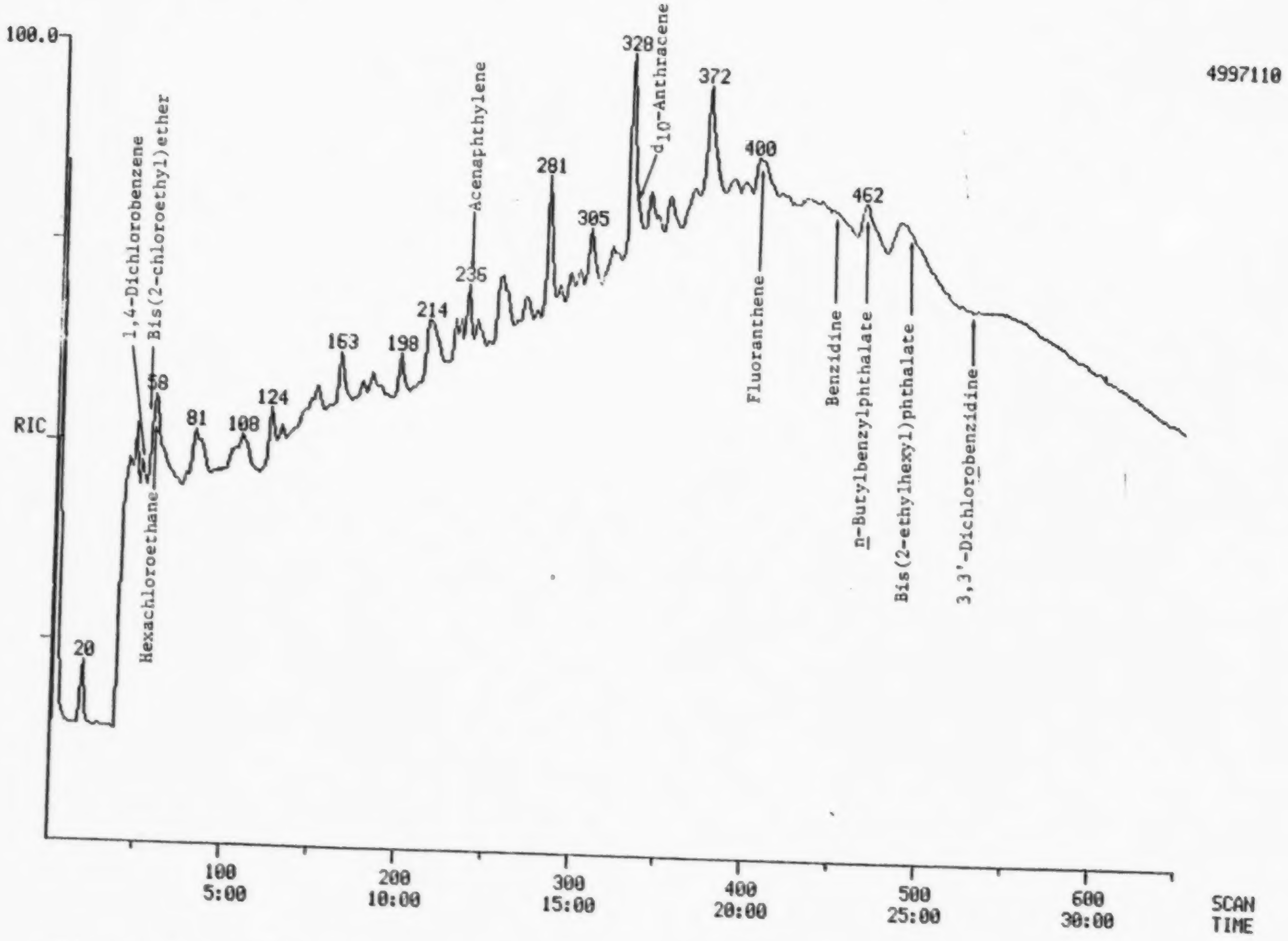

Figure 47. GC/MS chromatogram for base/neutrals in Platte County primary POTW sludge spiked at 4,000 µg/L with selected compounds.

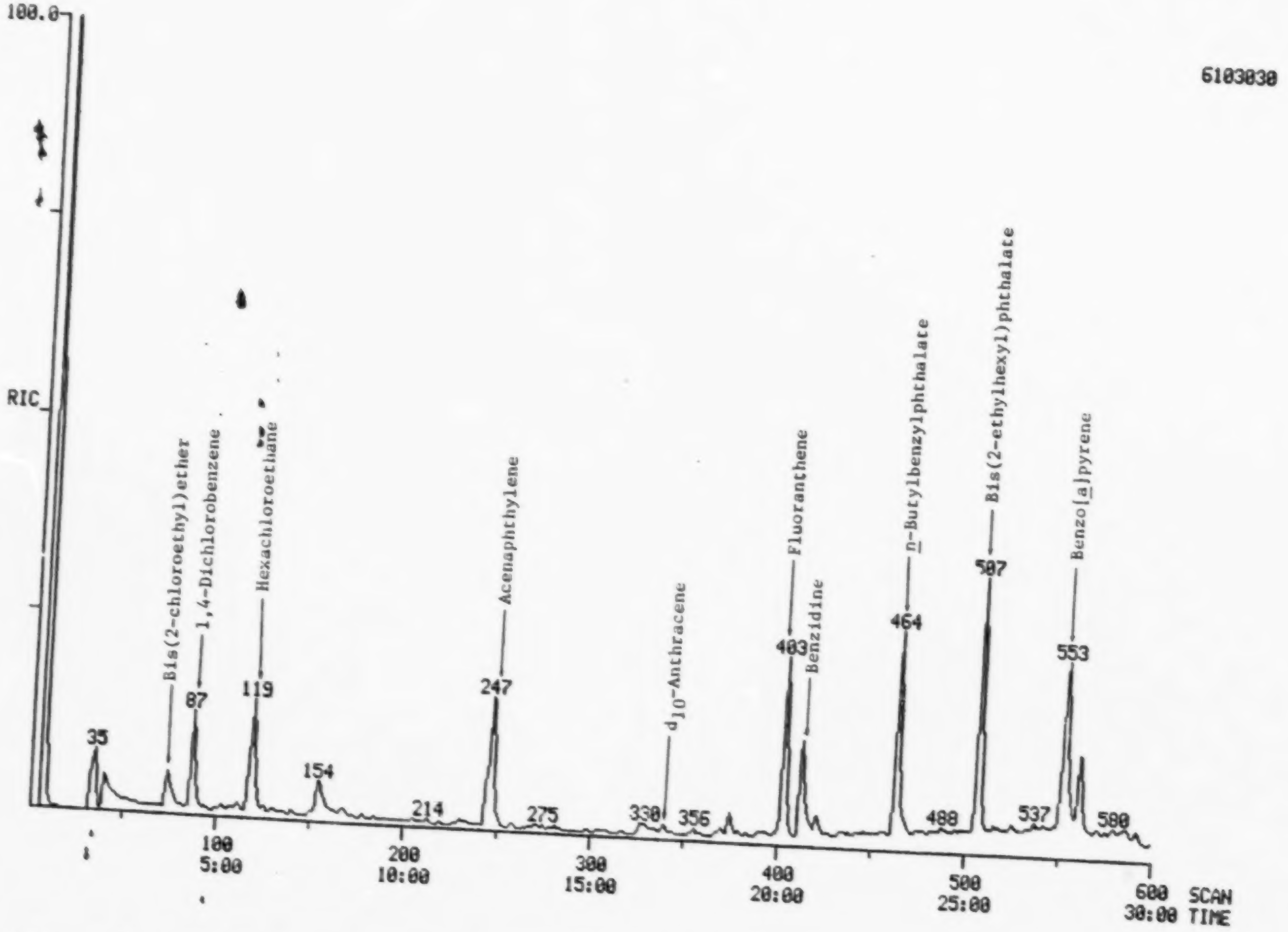

Figure 48. GC/MS chromatogram for base/neutrals in Platte County primary POTW sludge spiked at 40,000 μg/L with selected compounds.

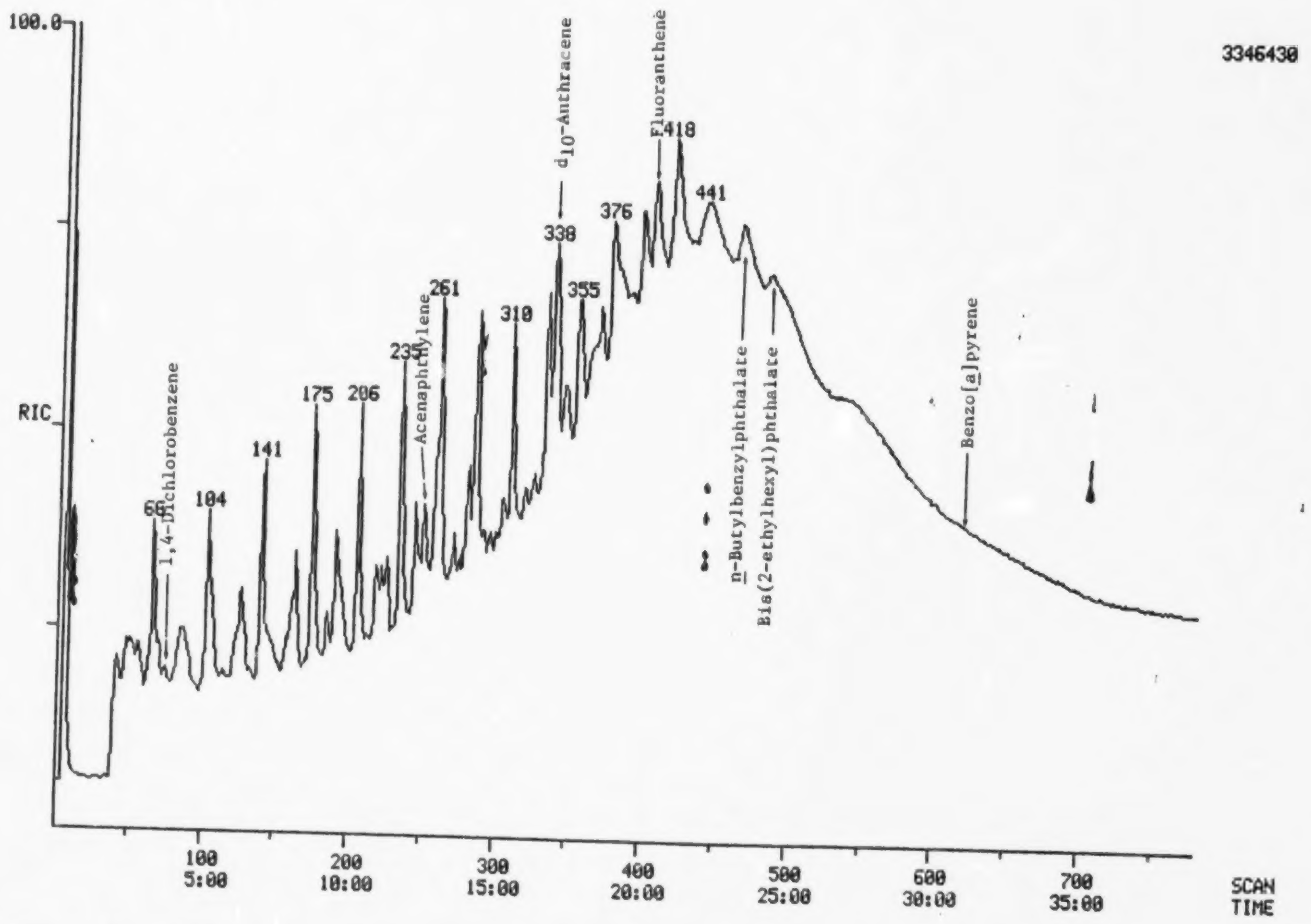

Figure 49. GC/MS chromatogram for base/neutrals in unspiked Blue River primary POTW sludge.

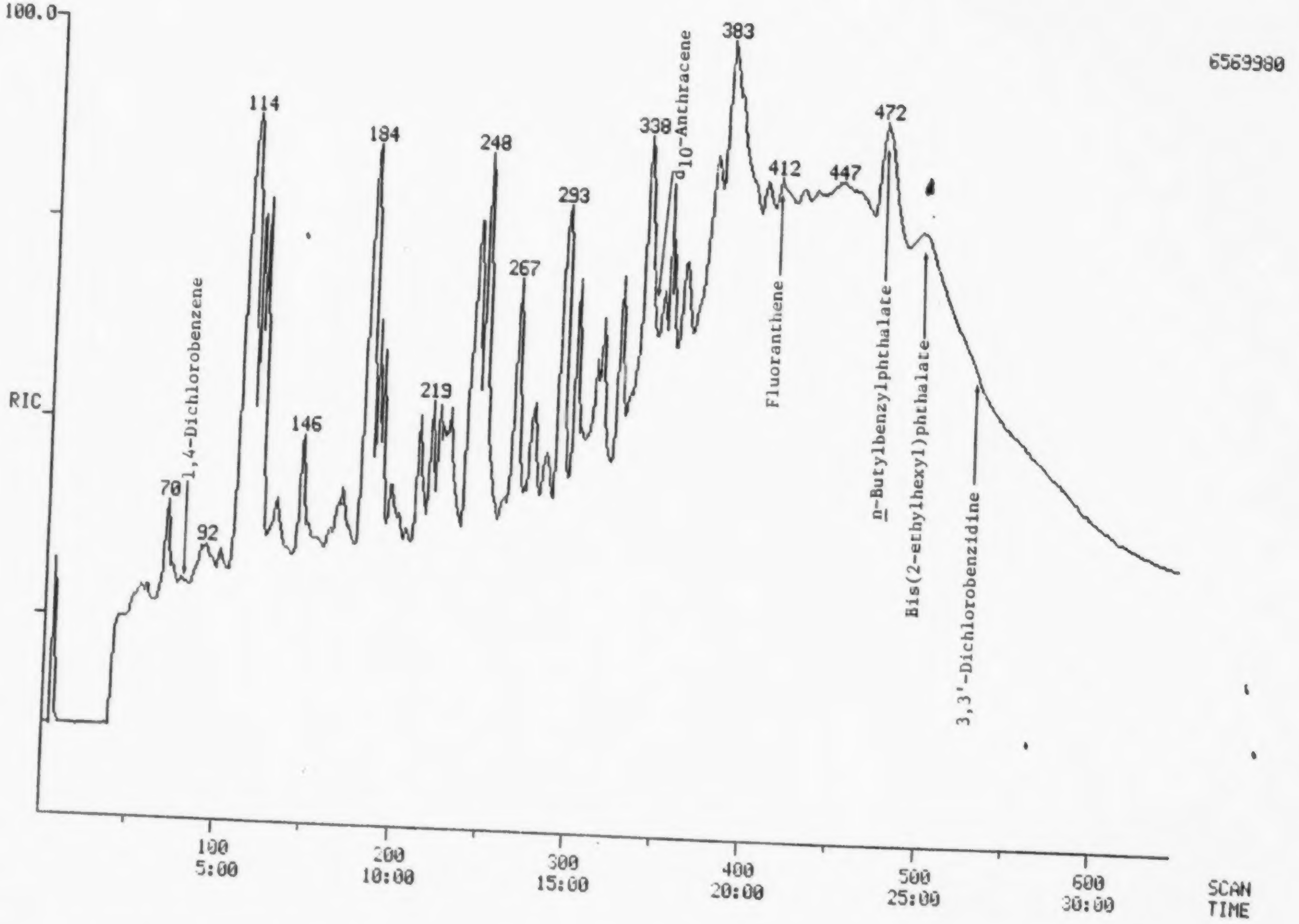

Figure 50. GC/MS chromatogram for base/neutrals in unspiked Kansas City, Kansas, primary POTW sludge.

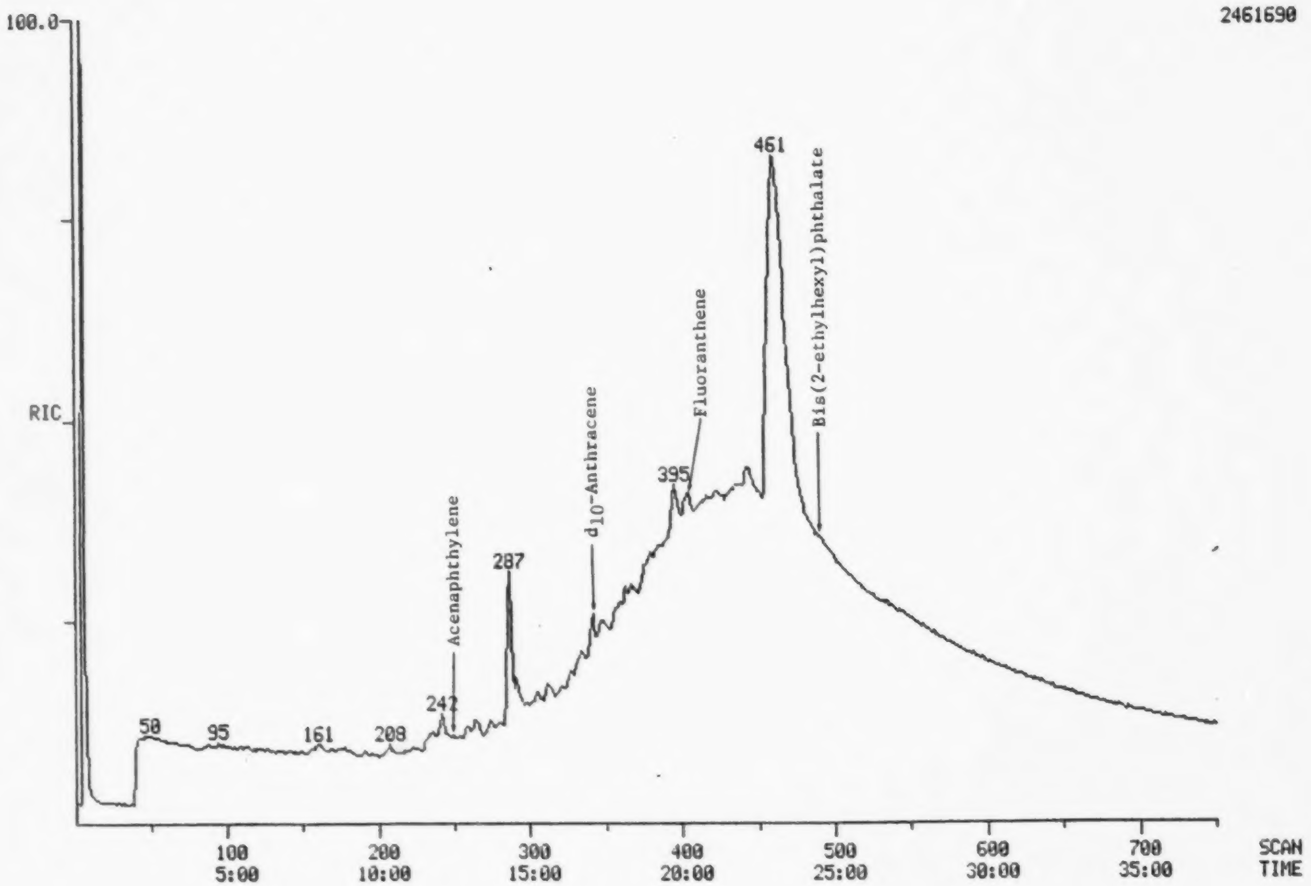

Figure 51. GC/MS chromatogram for base/neutrals in unspiked Industrial No. 1 primary sludge.

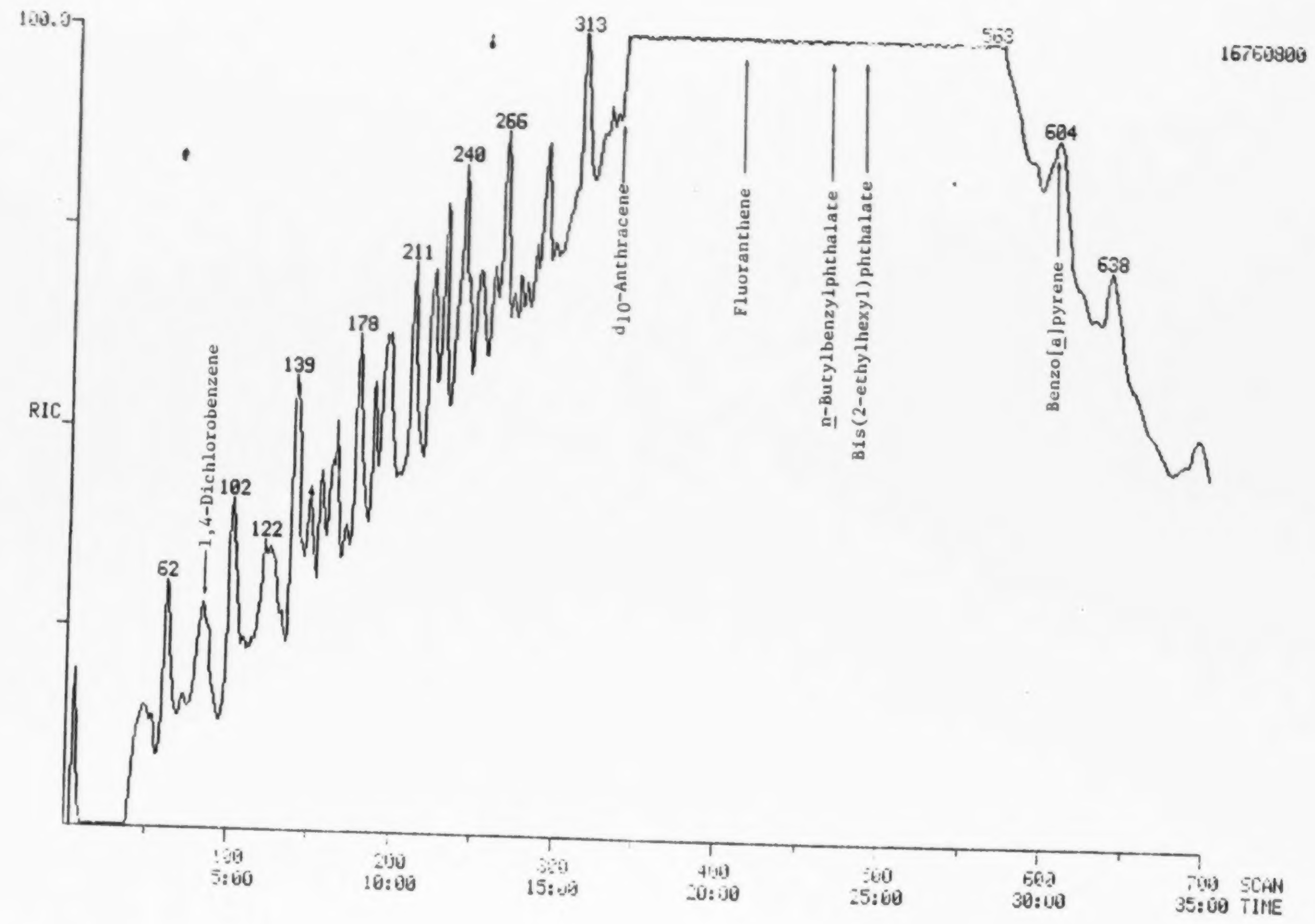

Figure 52. GC/MS chromatogram for base/neutrals in unspiked Industrial No. 2 primary sludge.

TABLE 53. RESULTS OF PRECISION AND ACCURACY EVALUATIONS FOR THE EXTRACTABLES METHOD (CAPILLARY COLUMN GC/MS) APPLIED TO THE ANALYSIS OF BASE/NEUTRAL COMPOUNDS IN MUNICIPAL AND INDUSTRIAL WASTEWATER TREATMENT SLUDGES

		Platte County POWW			Blue River POTW			Kansas City, Ks			Industrial No. 1			Industrial No. 2	
Compound	Spike conc. (µg/L)	Unspiked[a] sludge (µg/L)	Recovery (%)	Spike conc. (µg/L)	Unspiked[a] conc. (µg/L)	Recovery (%)	Spike conc. (µg/L)	Unspiked[a] conc. (µg/L)	Recovery (%)	Spike conc. (µg/L)	Unspiked[a] conc. (µg/L)	Recovery (%)	Spike conc. (µg/L)	Unspiked[a] conc. (µg/L)	Recovery (%)
1,4-Dichlorobenzene	417	21	52 ± 36[b]	400	ND[c]	9 ± 2	400	6	21 ± 12	400	ND	24 ± 5	400	58	23 ± 12
	4,160		100 ± 1	4,000		35 ± 14	4,000		41 ± 20	4,000		160 ± 97	4,000		57 ± 8
	39,990		62 ± 28	39,900		58 ± 8	39,990		55 ± 18	39,990		55 ± 8	40,000		70 ± 19
Hexachloroethane	441	ND	21 ± 14	400	ND	3 ± 1	400	ND	0	400	ND	7 ± 10	400	ND	3 ± 2
	4,400		22 ± 6	4,000		10 ± 4	4,000		15 ± 7	4,000		161 ± 100	4,000		75 ± 1
	40,010		46 ± 12	40,010		39 ± 6	40,010		42 ± 6	39,990		49 ± 21	40,000		35 ± 5
Bis(2-chloroethyl)-ether	408	ND	78 ± 83	400	ND	24 ± 15	400	ND	45 ± 30	400	ND	38 ± 9	400	ND	0
	4,070		140 ± 16	4,000		69 ± 32	4,000		130 ± 66	4,000		130 ± 56	4,000		63 ± 2
	39,990		130 ± 81	39,990		130 ± 66	39,990		240 ± 66	40,000		100 ± 8	40,000		92 ± 19
Acenaphthylene	411	ND	140 ± 72	400	34	18 ± 6	400	11	82 ± 46	400	ND	55 ± 5	400	730	d
	4,090		230 ± 39	4,000		53 ± 2	4,000		150 ± 51	4,000		110 ± 35	4,000		93 ± 3
	40,000		88 ± 26	40,000		110 ± 4	40,000		110 ± 9	39,990		100 ± 2	40,000		114 ± 27
2,6-Dinitrotoluene	407	ND	43 ± 27	400	ND	7 ± 6	400	ND	0	400	ND	11 ± 13	400	1,090	d
	4,050		5 ± 1	4,000		4 ± 4	4,000		16 ± 28	4,000		160 ± 80	4,000		62 ± 8
	40,040		78 ± 5	40,040		41 ± 43	40,040		76 ± 21	39,990		90 ± 3	40,000		121 ± 32
Fluoranthene	428	27	230 ± 122	400	750	7 ± 2[d]	400	131	110 ± 69	400	ND	67 ± 3	400	125	0
	4,270		190 ± 26	4,000		120 ± 8	4,000		120 ± 33	4,000		160 ± 64	4,000		121 ± 6
	40,000		89 ± 23	40,000		120 ± 10	40,000		110 ± 4	39,920		88 ± 19	40,000		120 ± 25
Benzidine	789	ND	0	800	ND	0	800	ND	6 ± 10	800	ND	0	780	ND	0
	7,870		1 ± 1	8,000		11 ± 4	8,000		1 ± 1	8,000		240 ± 100	7,800		35 ± 17
	80,000		40 ± 11	80,000		50 ± 10	80,000		81 ± 9	80,010		160 ± 6	70,000		53 ± 4
3,3'-Dichlorobenzidine	415	ND	5 ± 8	NA[e]			402	20	6 ± 1	NA		-	NA		-
	4,130		140 ± 32	NA			NA			NA		-	NA		-
	NA		-	NA		-	NA		-	NA		-	NA		-
n-Butylbenzylphthalate	452	770	290 ± 165[d]	400	2,380	80 ± 26[d]	400	5,230	f	400	ND	67 ± 8	400	9,930	f
	4,51[illegible]		160 ± 26	4,000		72 ± 20	4,000		280 ± 266[d]	4,000		230 ± 36	4,000		d
	40,0[illegible]0		120 ± 16	40,000		120 ± 19	40,000		310 ± 11	40,000		72 ± 18	40,000		140 ± 35
Di-n-octylphthalate	444	3,500	d	400	3,380	d	400	1,800	d	400	54	58 ± 16	490	2,350	d
	4,430		150 ± 47	4,000		18 ± 18	4,000		200 ± 91	4,000		140 ± 66	4,890		170 ± 24
	40,0[illegible]0		130 ± 57	40,0[illegible]0		99 ± 11	40,010		190 ± 16	40,000		58 ± 13	48,820		210 ± 62
Benzo[a]pyrene	406	84	350 ± 202	400	540	63 ± 39[d]	400	ND	110 ± 51	400	ND	26 ± 2	400	910	d
	4,050		100 ± 21	4,000		46 ± 13	4,000		120 ± 24	4,000		170 ± 110	4,000		57 ± 14
	40,010		140 ± 25	40,010		110 ± 29	40,010		170 ± 13	40,080		42 ± 13	40,000		110 ± 22

[a] Mean of two determinations.

[b] Mean ± standard deviation for three determinations.

[c] ND = not detected.

[d] Concentration determined in the unspiked sludge was higher than the spike level.

[e] NA = this compound was not available when these samples were spiked.

[f] Concentration determined in the unspiked sludge was 10 times higher than the spike level.

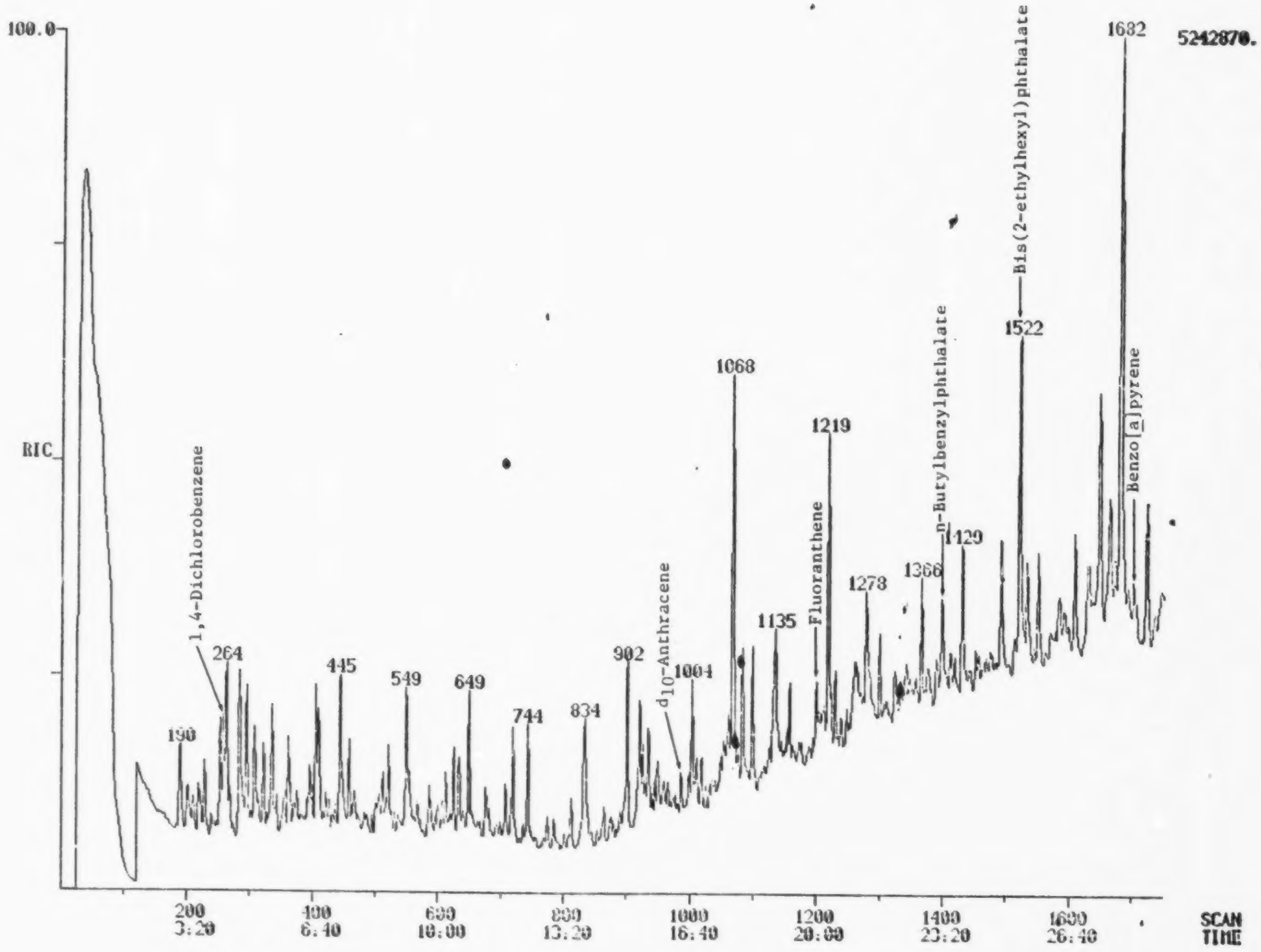

Figure 53. HRGC/MS chromatogram for base/neutrals in unspiked Platte County primary POTW sludge.

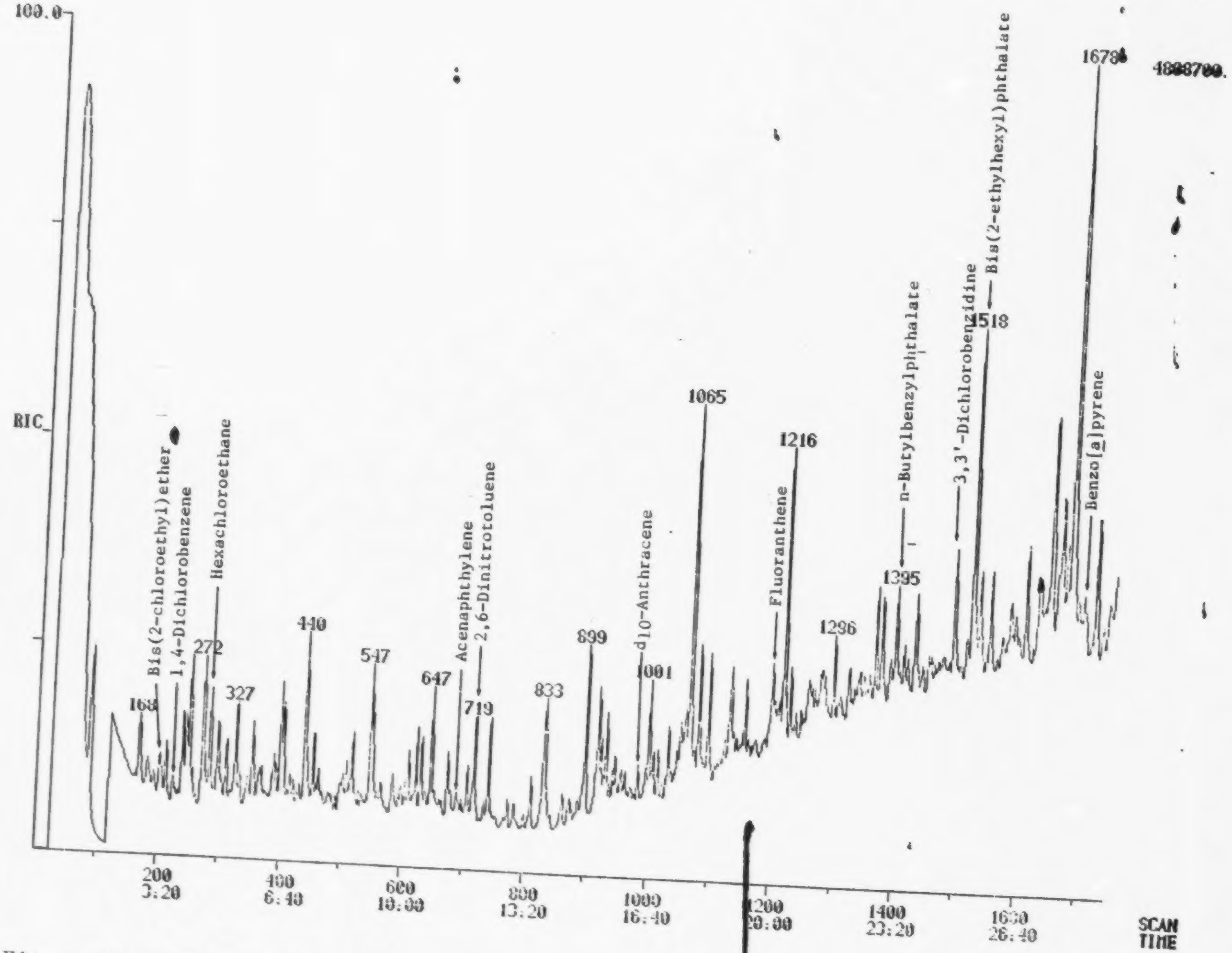

Figure 54. HRGC/MS chromatogram for base/neutrals in Platte County primary POTW sludge spiked at 400 μg/L with selected compounds.

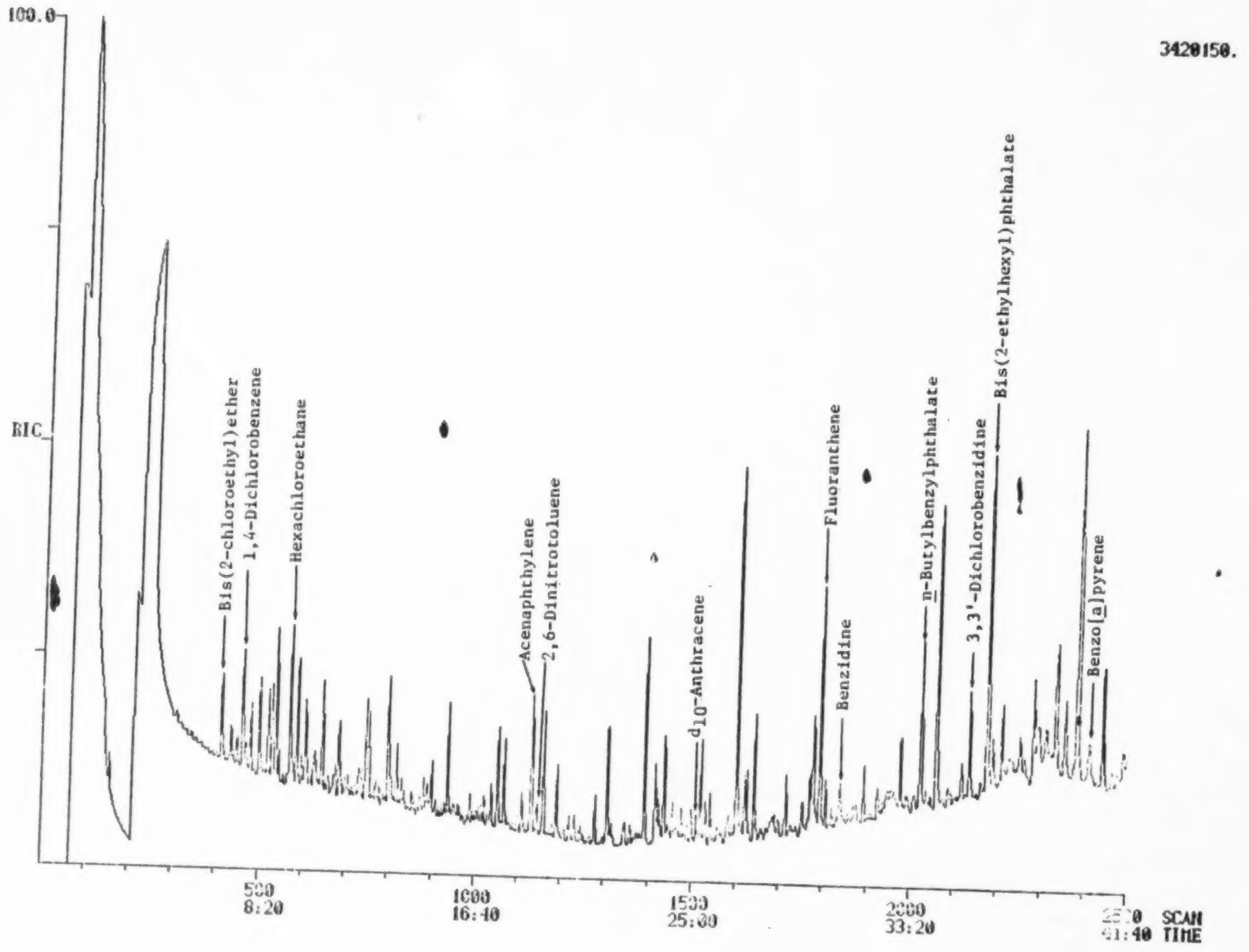

Figure 55. HRGC/MS chromatogram for base/neutrals in Platte County primary POTW sludge spiked at 4,000 µg/L with selected compounds.

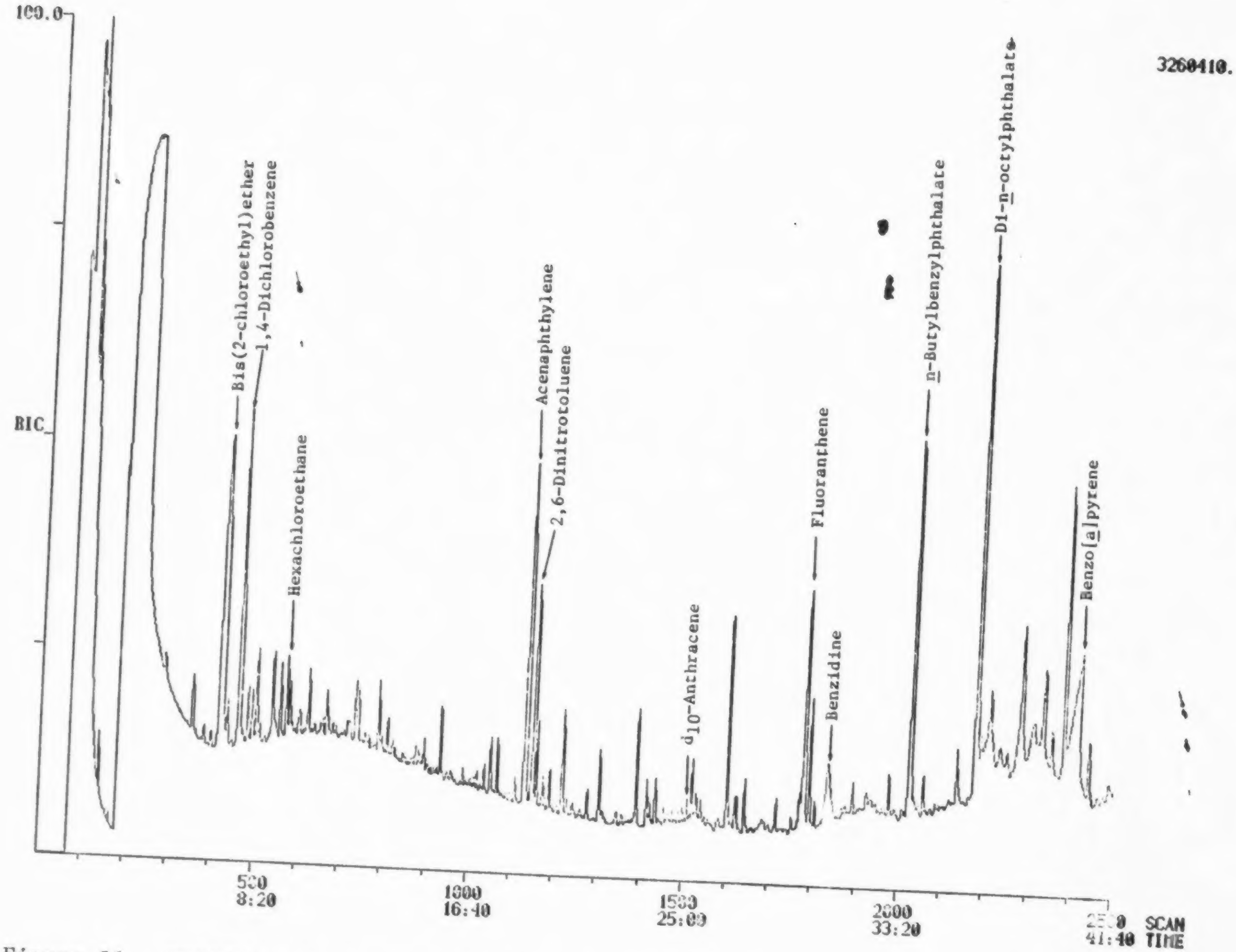

Figure 56. HRGC/MS chromatogram for base/neutrals in Platte County primary POTW sludge spiked at 40,000 μg/L with selected compounds.

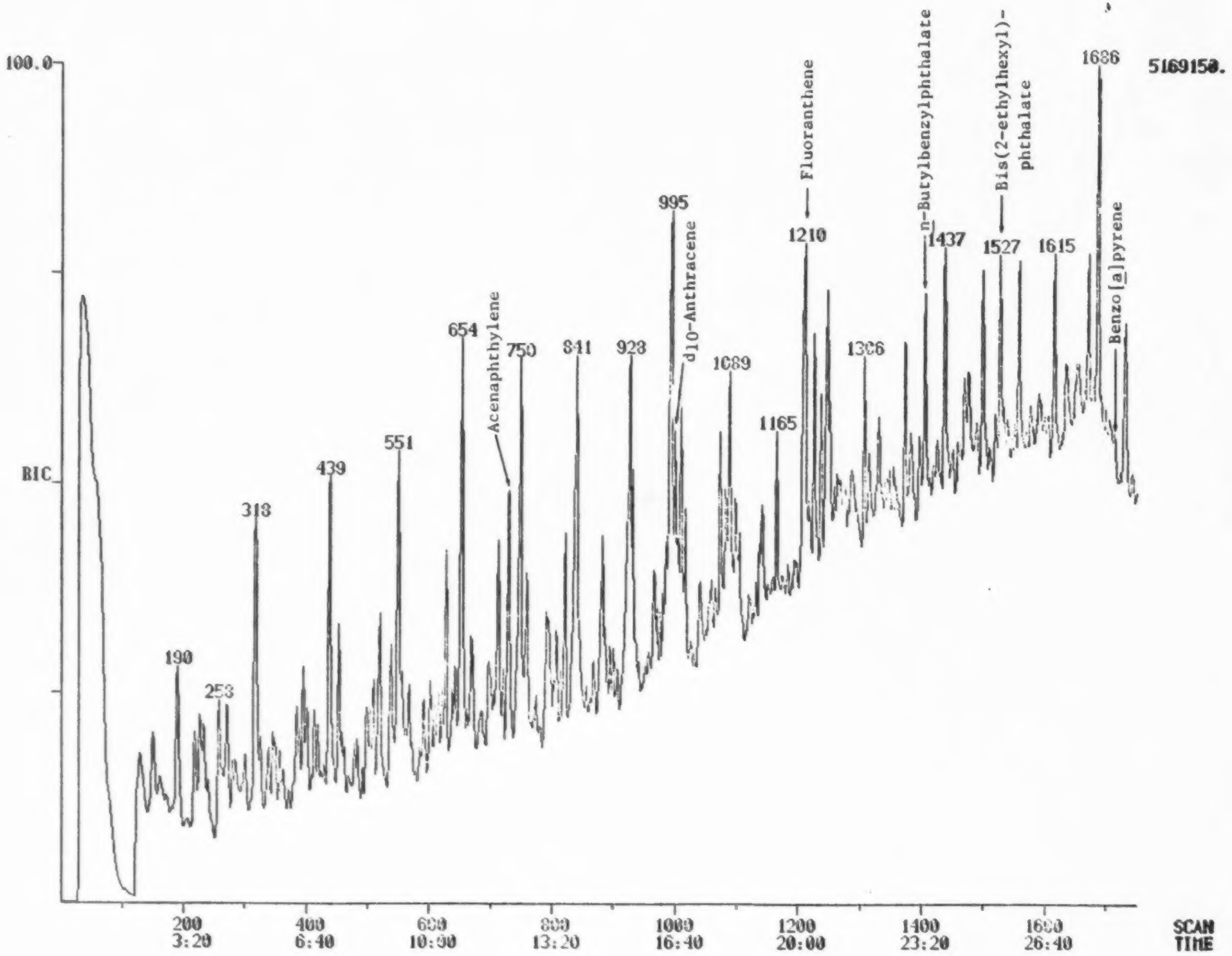

Figure 57. HRGC/MS chromatogram for base/neutrals in unspiked Blue River primary POTW sludge.

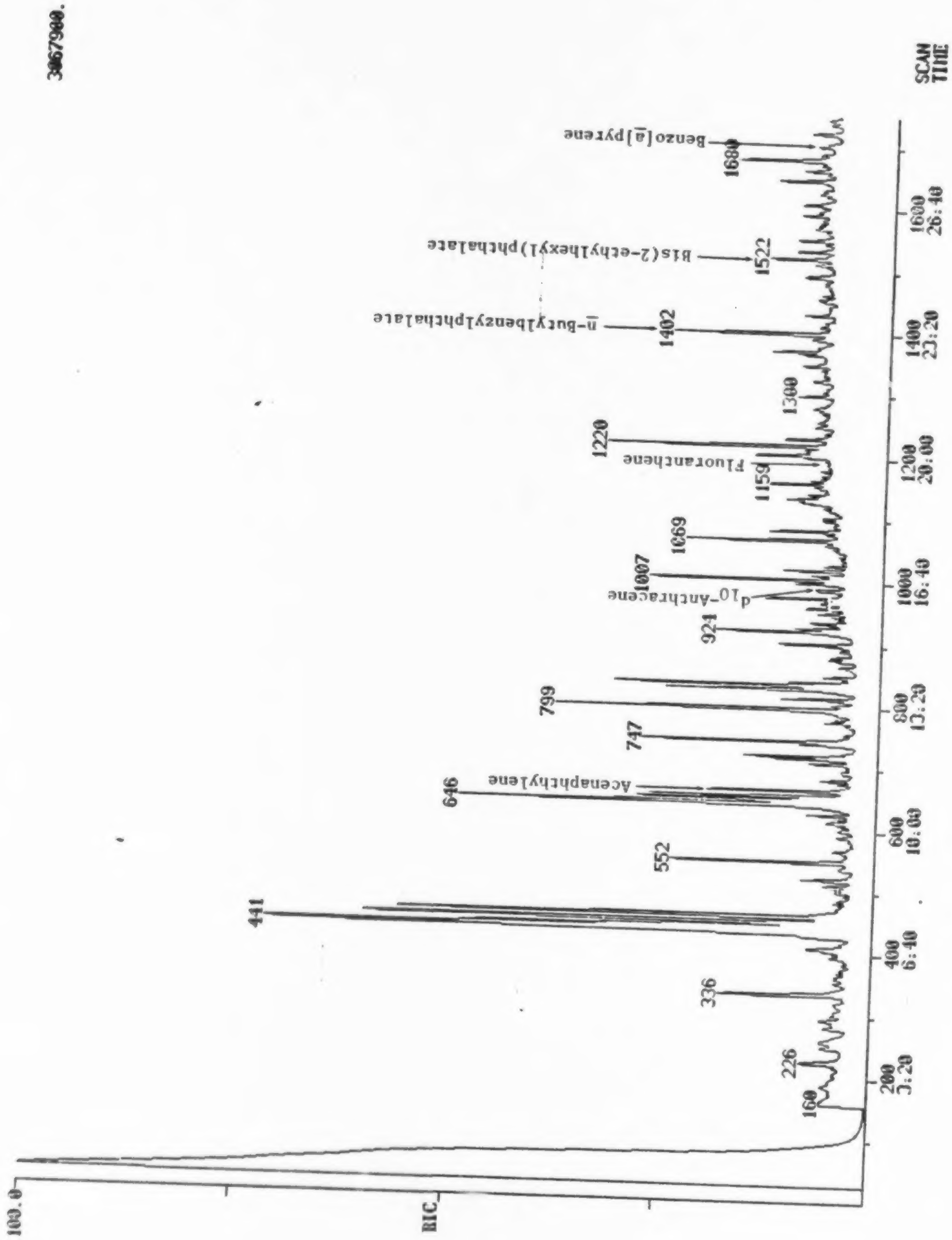

Figure 58. HRGC/MS chromatogram for base/neutrals in unspiked Kansas City, Kansas, primary POTW sludge.

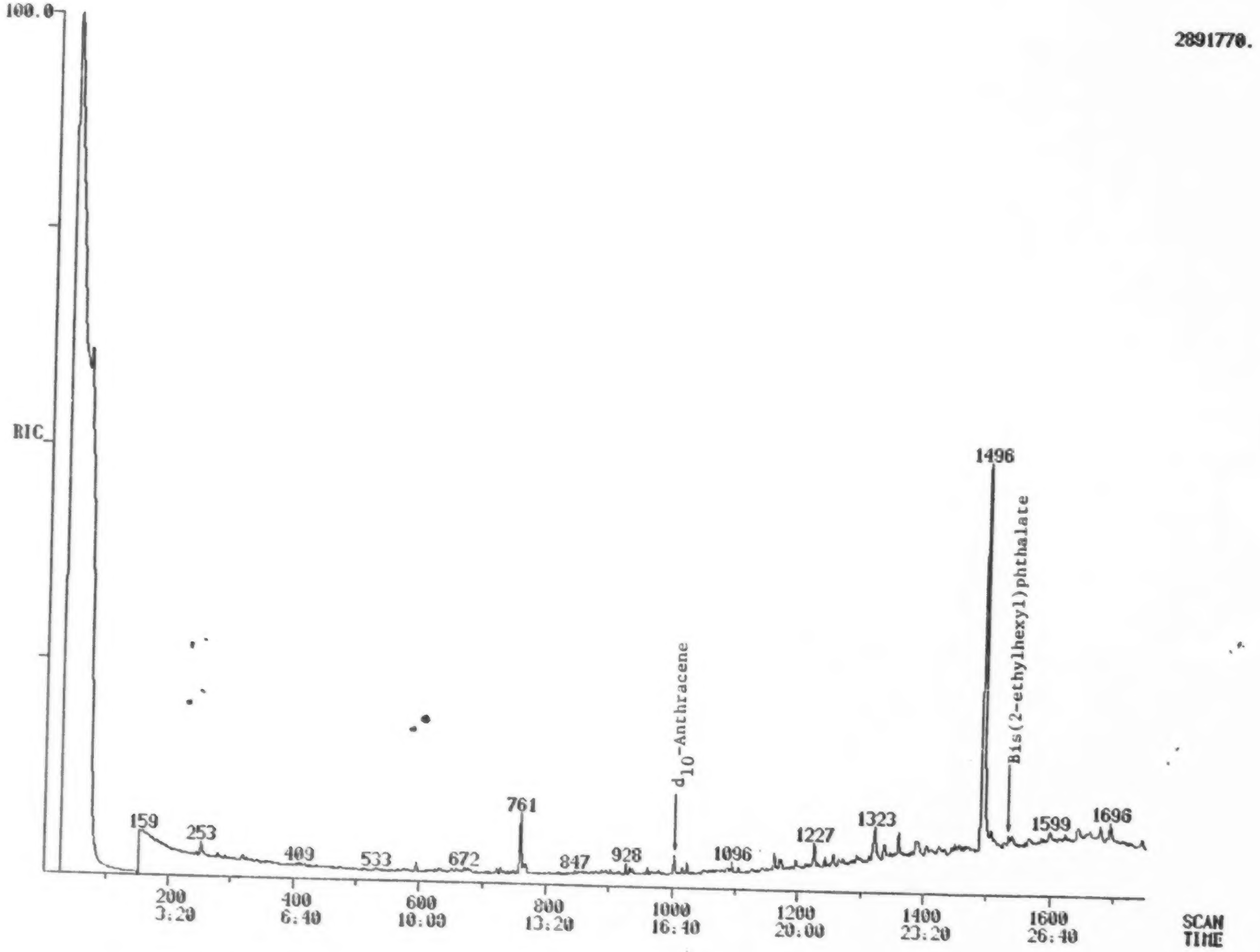

Figure 59. HRGC/MS chromatogram for base/neutrals in unspiked Industrial No. 1 primary sludge.

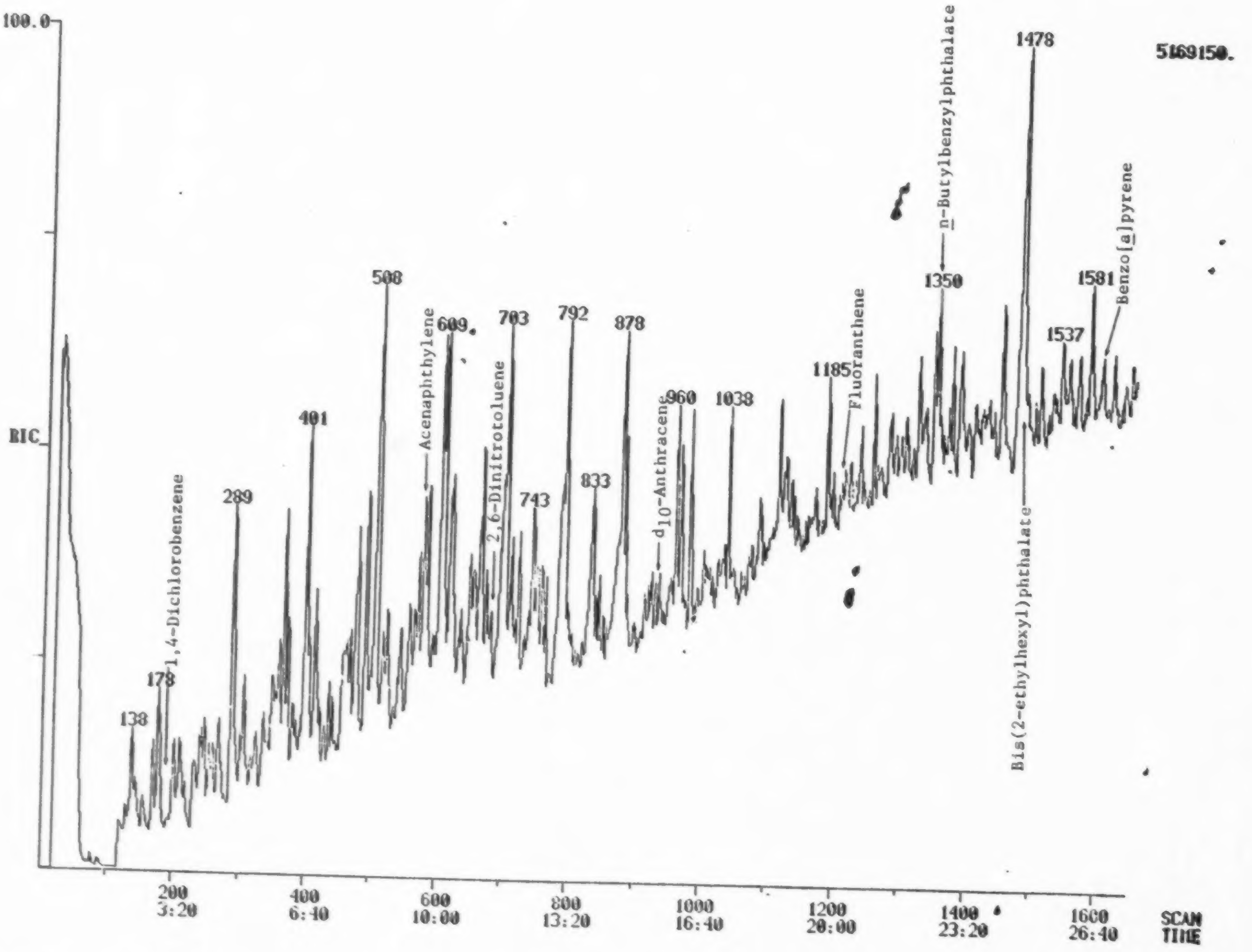

Figure 60. HRGC/MS chromatogram for base/neutrals in unspiked Industrial No. 2 primary sludge.

The recoveries determined for the acidic compounds are shown in Table 54. Figures 61 to 68 show the GC/MS chromatograms for spiked and unspiked Kansas City, Kansas, POTW sludge and for unspiked sludges from the remaining four plants. The recoveries observed were generally good and were reproducible. No zero recoveries were observed. Although many of the spike levels were lower than the unspiked concentrations, 65% of all recoveries were in the range of 50 to 150%, 21% were less than 50%, and 14% were greater than 150% recovery. The RSD values were low for triplicate determinations, 70% were 30% or less RSD, and 40% were less than 10% RSD. Poor recoveries were determined for 2,4-dimethylphenol from the Platte County sludge samples. Recoveries observed for this compound during the method development experiments were frequently anomalously low. This may indicate that 2,4-dimethylphenol is susceptible to biodegradation in some sludges.

In view of the complexity and diversity of municipal and industrial wastewater treatment sludges, the precision and accuracy results presented here demonstrate that the protocol developed can be reliably applied to the analysis of the organic priority pollutants in sludge. The success of this protocol for the variety of extractable compounds for which it was developed and evaluated indicates that the methods included may also be useful for many nonpriority pollutant analytes.

TIME/COST ANALYSIS OF THE METHOD

Unlike the similarity of the time/costs for conducting purgeables analyses of sludge and wastewater, the time/costs for the extractable compounds are considerably higher for sludge analyses than for wastewater analyses. However, the same conditions and assumptions are applicable for the estimates presented here. The analysts are experienced professionals, no major equipment purchases are included, samples are analyzed in lots of 20 to 100, and analytical standards are prepared from commercially available mixed solutions.

The estimated per sample labor and cost requirements for analysis of extractable priority pollutants in sludges are shown in Table 55. The acidic compounds are analyzed in the same manner in both options, i.e., extract cleanup by GPC and analysis by packed column GC/MS. The two cost options shown in Table 55 are for the two principal analytical options for the B/N compounds. The labor and costs for analysis of spiked and replicate samples, sample compositing and spiking, and reanalysis of selected extracts must also be estimated for each specific analysis program.

TABLE 54. RESULTS OF PRECISION AND ACCURACY EVALUATIONS FOR THE EXTRACTABLES METHOD APPLIED TO THE ANALYSIS OF ACIDIC COMPOUNDS IN MUNICIPAL AND INDUSTRIAL WASTEWATER TREATMENT SLUDGES

	Platte County POWW			Blue River POTW			Kansas City, Ks			Industrial No. 1			Industrial No. 2		
Compound	Spike conc. (μg/L)	Unspiked[a] sludge (μg/L)	Recovery (%)	Spike conc. (μg/L)	Unspiked[a] conc. (μg/L)	Recovery (%)	Spike conc. (μg/L)	Unspiked[a] conc. (μg/L)	Recovery (%)	Spike conc. (μg/L)	Unspiked[a] conc. (μg/L)	Recovery (%)	Spike conc. (μg/L)	Unspiked[a] conc. (μg/L)	Recovery (%)
Phenol	464	323	86 ± 14[b]	400	160	67 ± 22	400	2,800	c	400	112	48 ± 9	400	800	101 ± 48
	4,630		52 ± 8	4,000		89 ± 8	4,000		72 ± 71	4,000		49 ± 6	4,000		47, 120
	46,280		69 ± 6	40,000		68 ± 15	40,000		78 ± 14	40,000		99, 88	40,000		57, 66
2,4-Dimethylphenol	412	ND[d]	7 ± 3	400	ND	94 ± 10	400	ND	174 ± 51	400	ND	88 ± 7	400	1,370	c
	4,110		4 ± 1	4,000		45 ± 2	4,000		21 ± 9	4,000		90 ± 11	4,000		94, 232
	41,080		5 ± 3	40,000		83 ± 68	40,000		110, 93			190, 190	40,000		25, 28
2,4-Dichlorophenol	399	ND	140 ± 5	400	72	140 ± 7	400	1,780	c	400	ND	69 ± 9	400	114	380 ± 95
	3,970		66 ± 13	4,000		93 ± 7	4,000		92 ± 64	4,000		53 ± 3	4,000		67, 140
	39,750		89 ± 8	40,000		78 ± 7	40,000		69 ± 17	40,000		102, 95	40,000		68, 79
Pentachlorophenol	401	323	130 ± 29	400	660	70 ± 10[c]	400	1,120	230, 230[c]	400	229	41 ± 20	400	13,960	e
	4,000		150 ± 27	4,000		88 ± 6	4,000		202 ± 75	4,000		45 ± 3	4,000		c
	40,010		79 ± 101	39,970		71 ± 12	39,970		85 ± 47	40,000		79, 68	40,000		39, 53

a Mean for two determinations.

b Mean ± standard deviation for three determinations.

c Concentration determined in the unspiked sludge was higher than the spike level.

d ND = not detected.

e Concentration determined in the unspiked sludge was 10 times higher than the spike level.

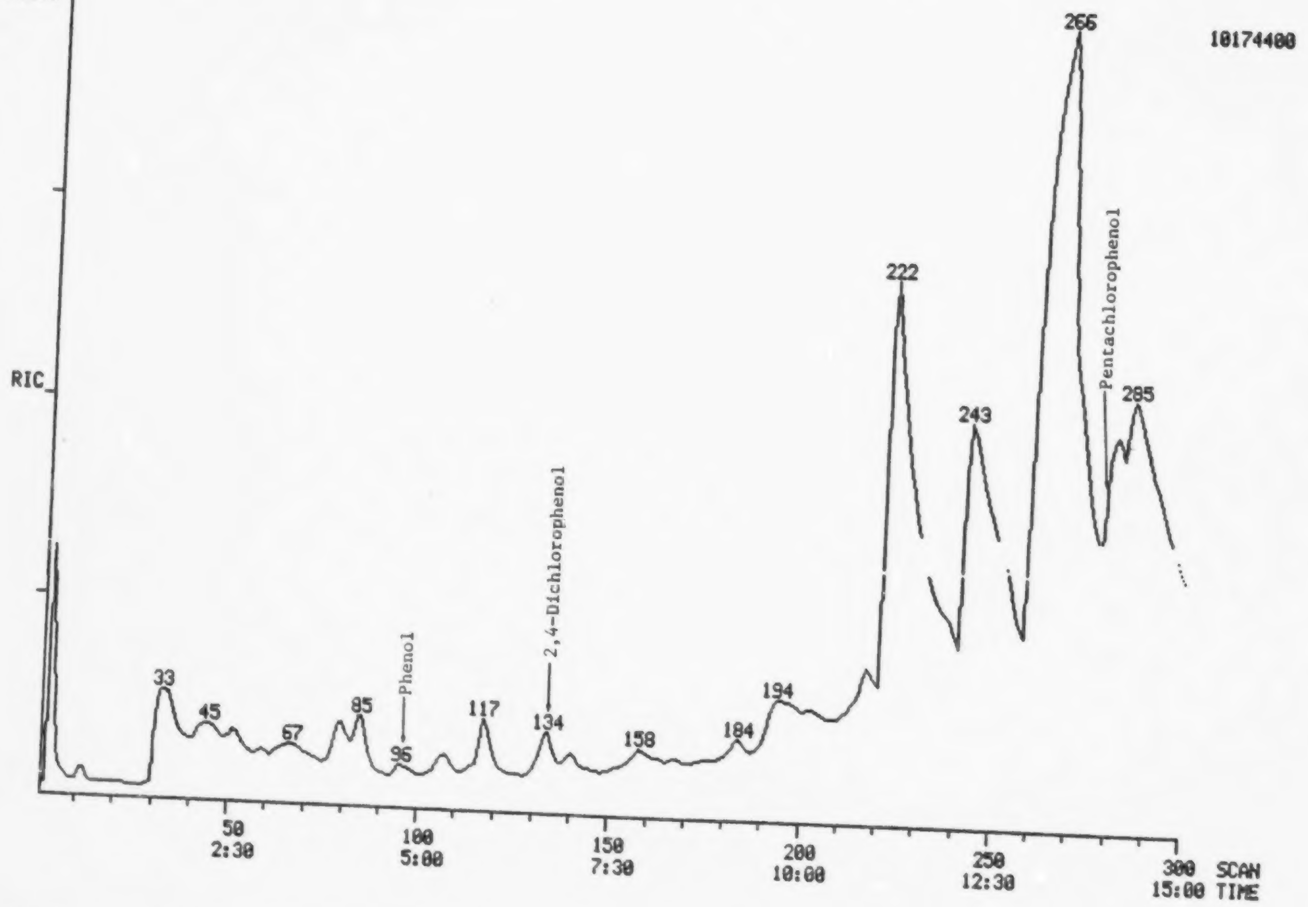

Figure 61. GC/MS chromatogram for acids in unspiked Kansas City, Kansas, primary POTW sludge.

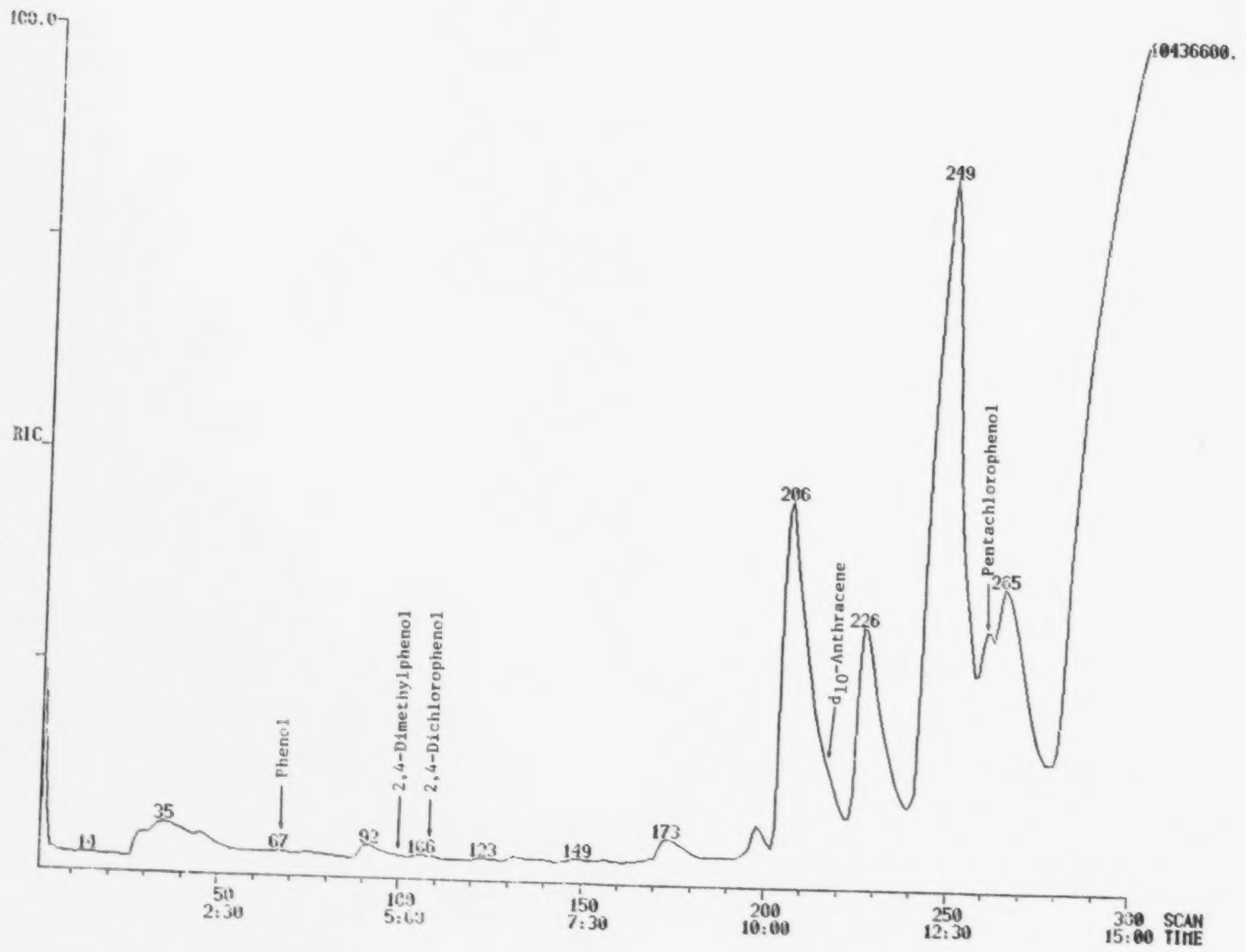

Figure 62. GC/MS chromatogram for acids in Kansas City, Kansas, primary POTW sludge spiked at 400 μg/L with selected compounds.

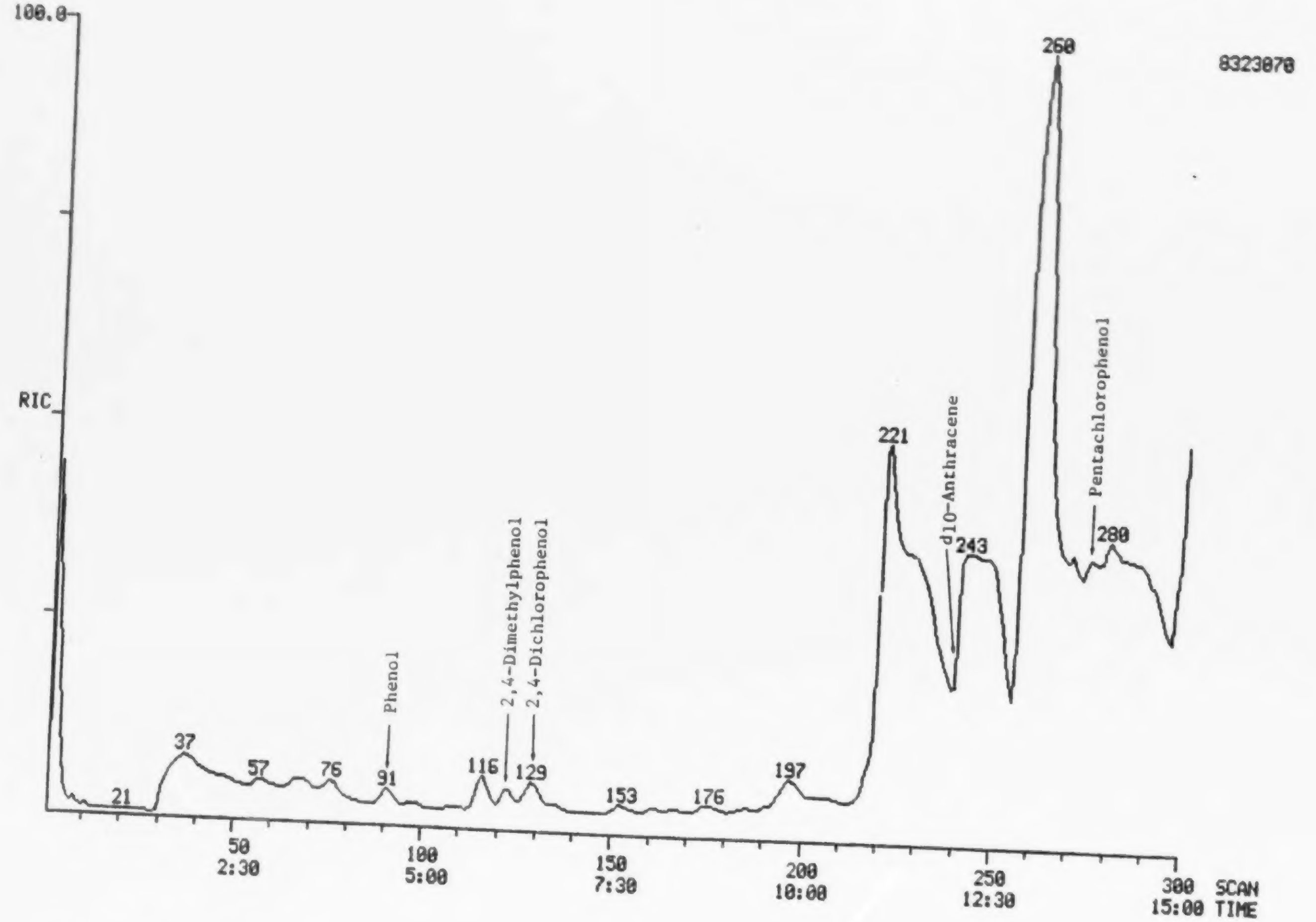

Figure 63. GC/MS chromatogram for acids in Kansas City, Kansas, primary POTW sludge spiked at 4,000 μg/L with selected compounds.

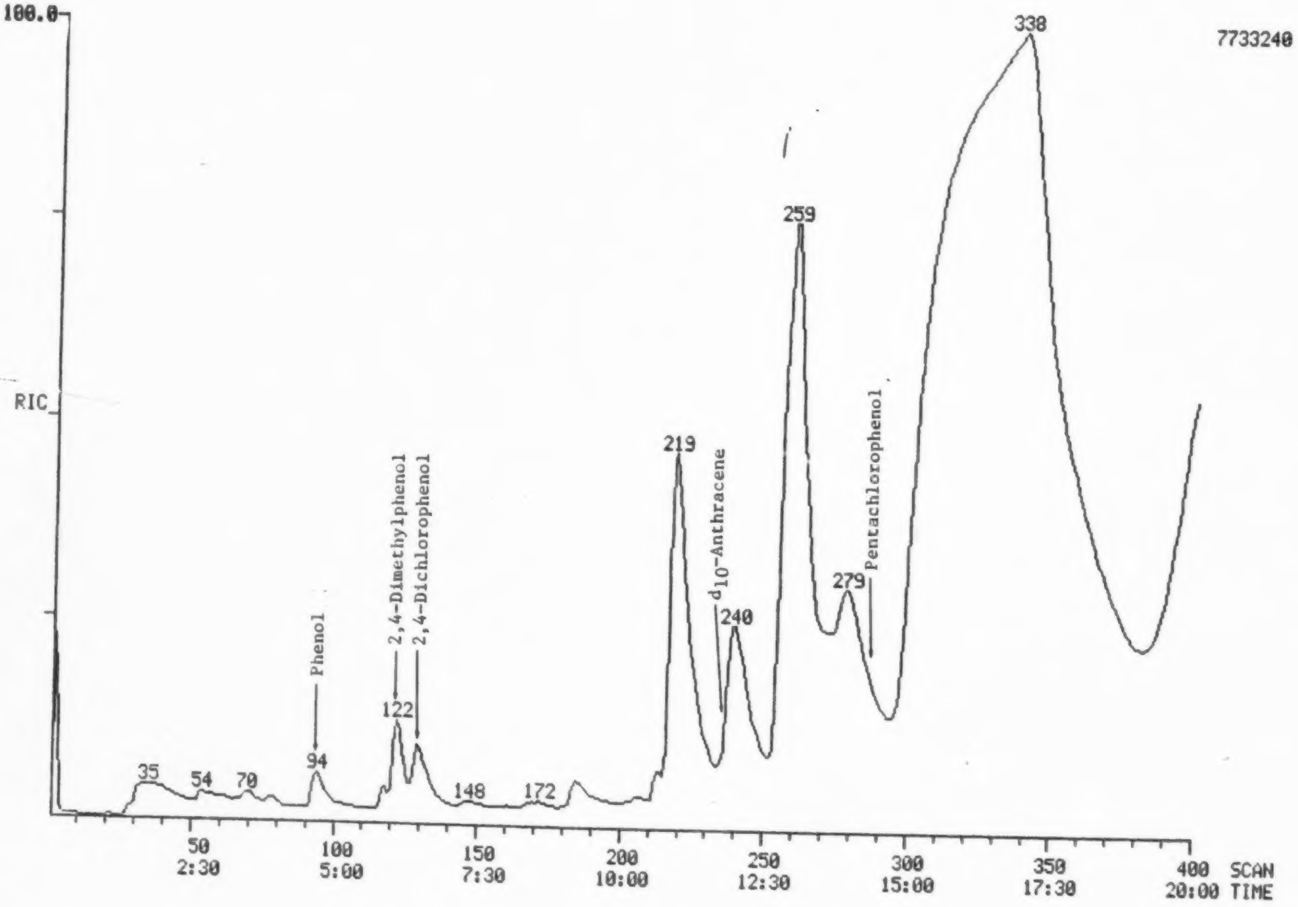

Figure 64. GC/MS chromatogram for acids in Kansas City, Kansas, primary POTW sludge spiked at 40,000 µg/L with selected compounds.

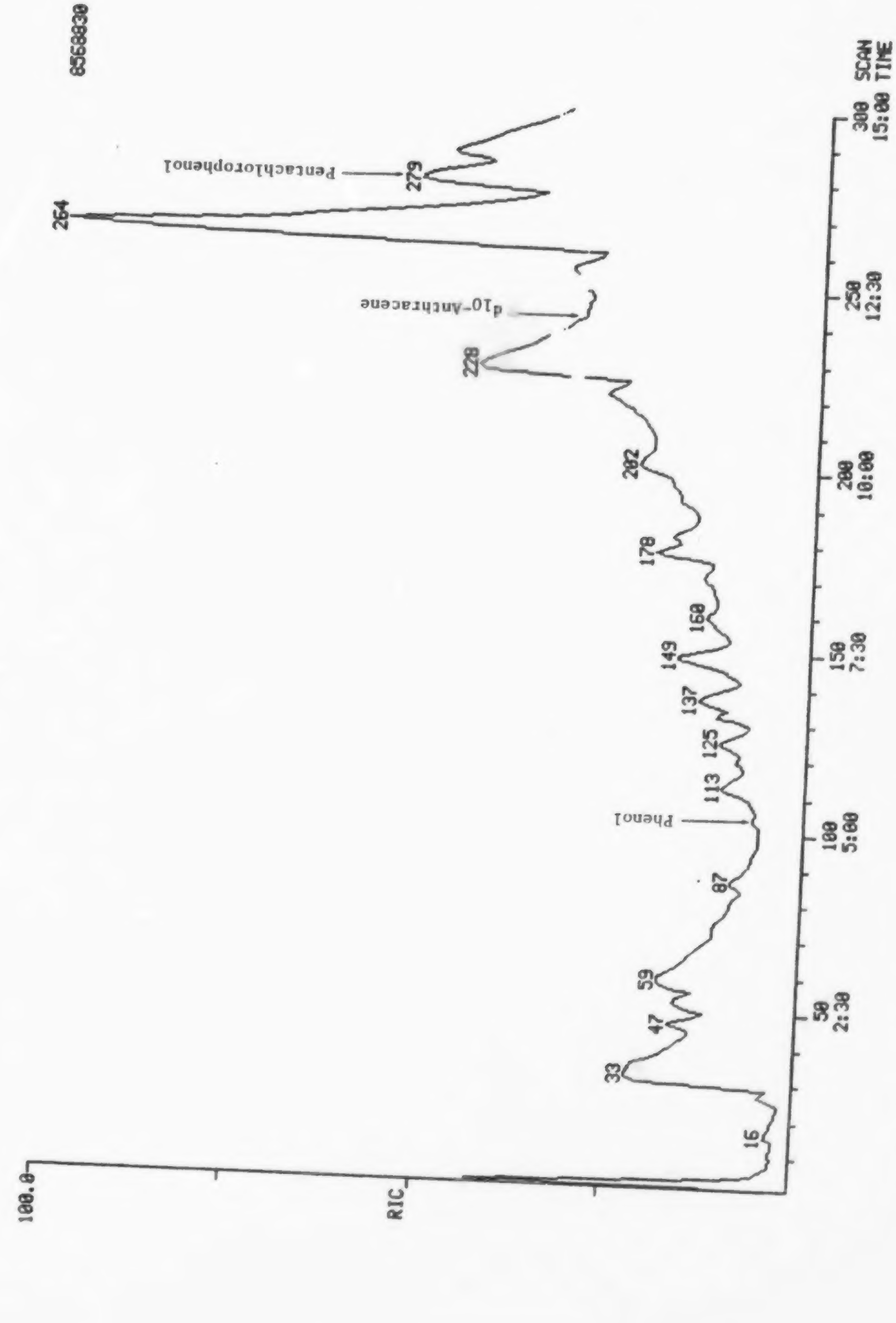

Figure 65. GC/MS chromatogram for acids in unspiked Platte County primary POTW sludge.

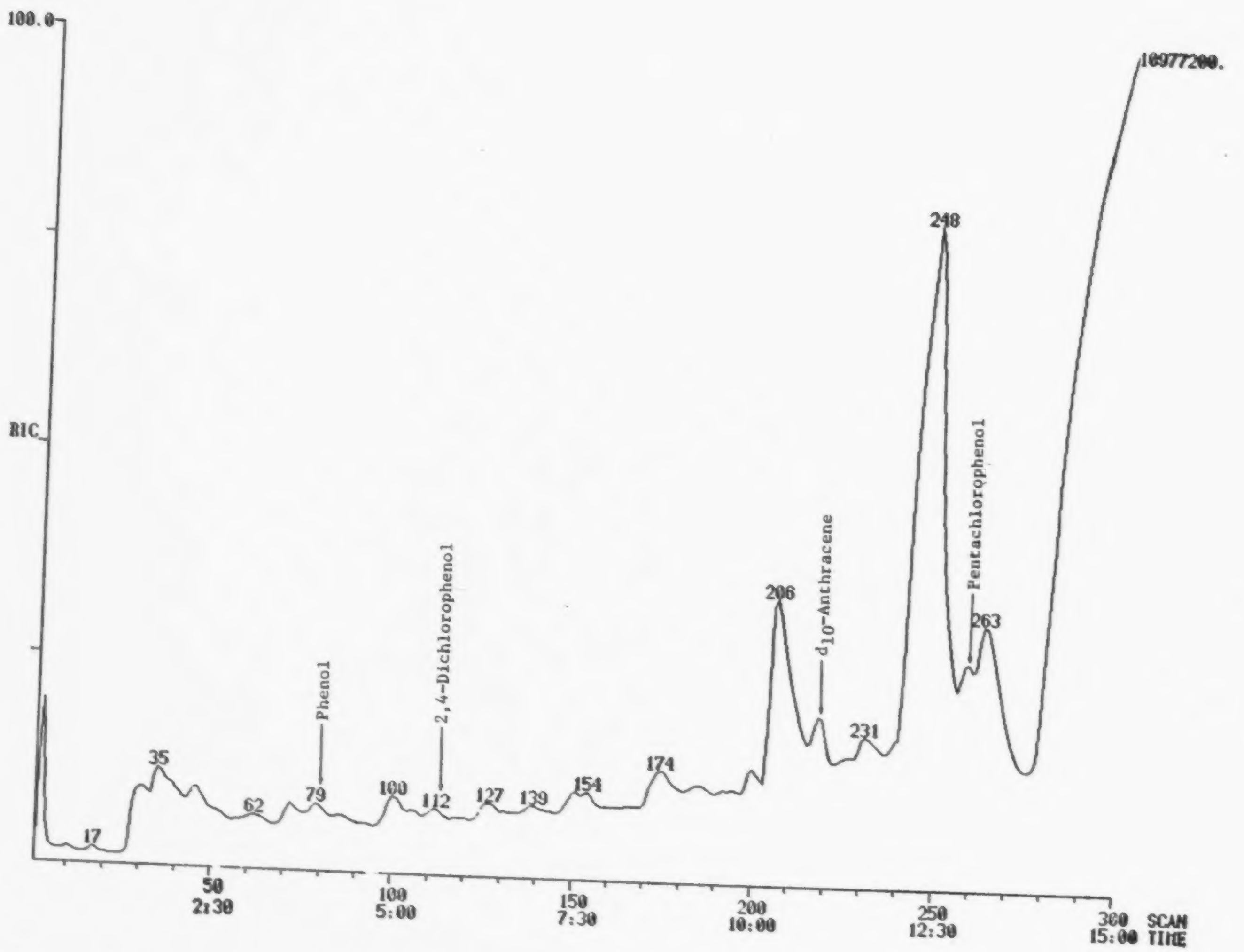

Figure 66. GC/MS chromatogram for acids in unspiked Blue River primary POTW sludge.

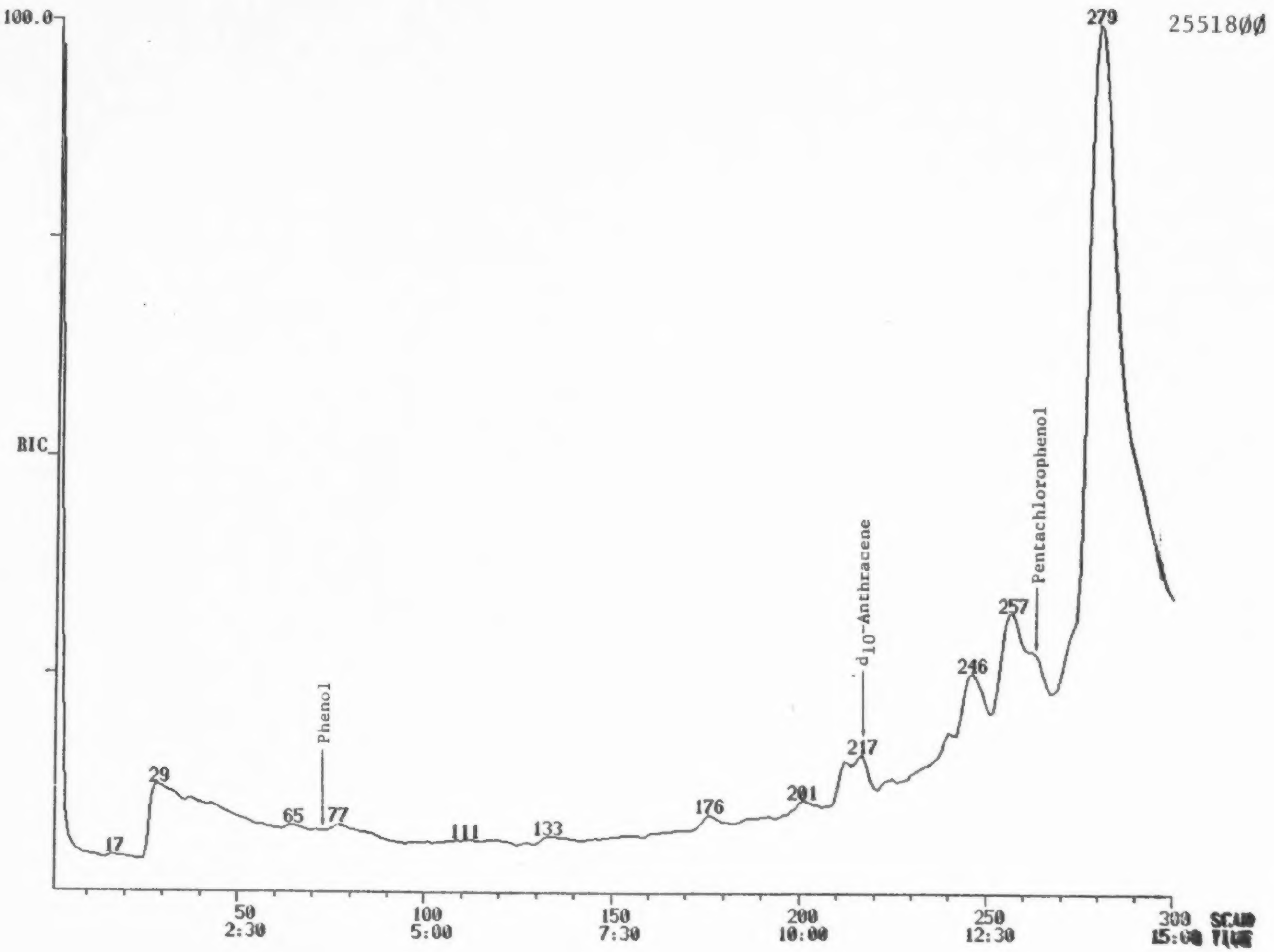

Figure 67. GC/MS chromatogram for acids in unspiked Industrial No. 1 primary sludge.

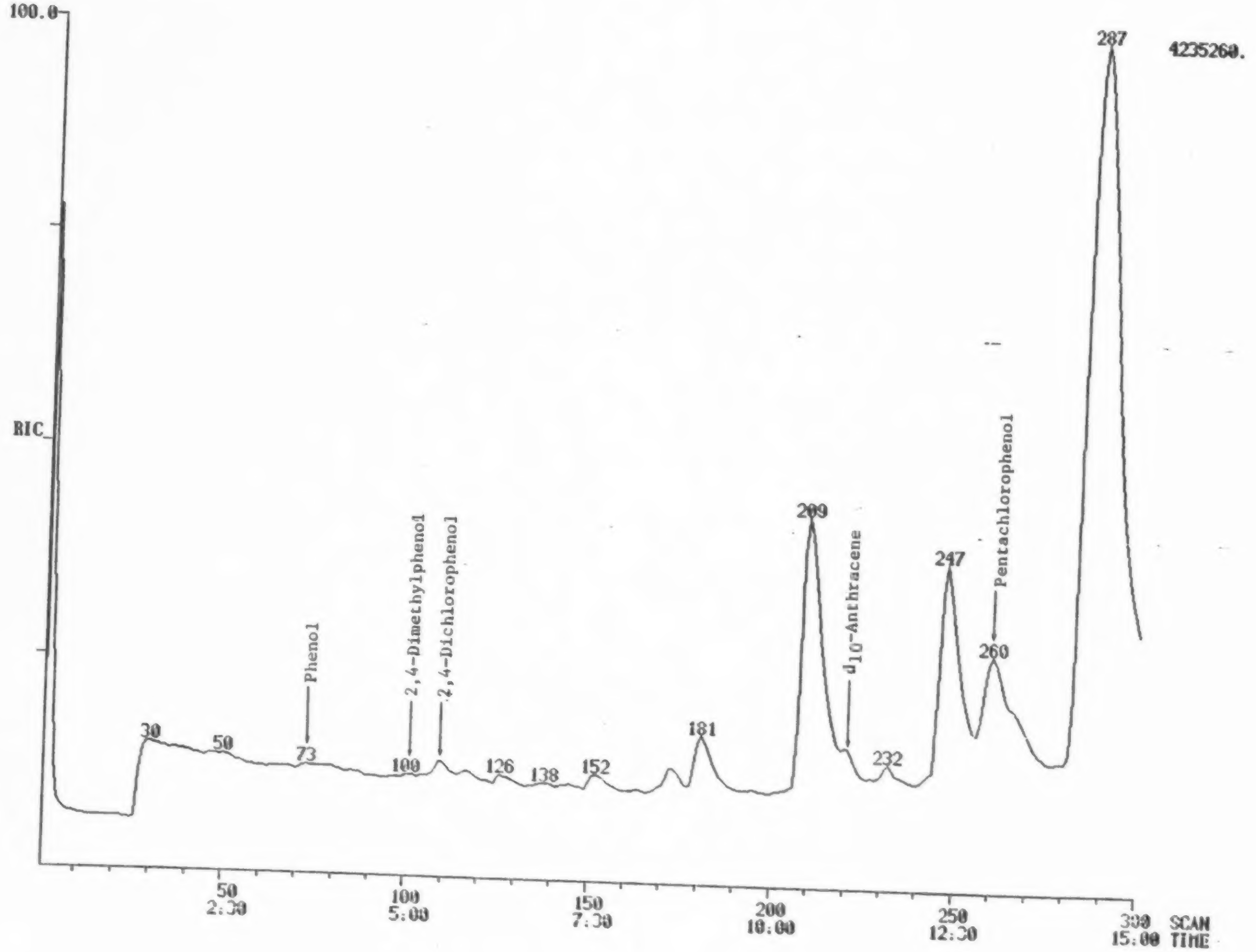

Figure 68. GC/MS chromatogram for acids in unspiked Industrial No. 2 primary sludge.

TABLE 55. TIME/COST ESTIMATE (PER SAMPLE) FOR ANALYSIS OF EXTRACTABLE COMPOUNDS IN SLUDGE

	Option A[a]			Option B[b]		
Operation	Labor (h)	GC/MS (h)	Other costs ($)	Labor (h)	GC/MS (h)	Other costs ($)
Extraction	4.8			4.8		
Extract cleanup						
GPC	0.4			0.7		
Florisil or silica gel	1.3					
GC/MS	2.7	2.7		2.5	2.5	
Data retrieval and interpretation	2.8			2.8		
Total	12.0	2.7	32	10.8	2.5	27

[a] B/N extracts cleaned up by florisil or silica gel chromatography and analyzed by capillary column GC/MS.

[b] B/N and acid extracts cleaned up by GPC and analyzed by packed column GC/MS.

SECTION 6

EVALUATION OF THE APPLICABILITY OF THE PRELIMINARY POTW SLUDGE PROTOCOL METHODS FOR SEDIMENT ANALYSIS

Following the development of the preliminary POTW sludge protocol,[4] the purging, extraction, and extract cleanup methods were briefly evaluated for their applicability for analysis of organic priority pollutants in sediments. Differences in the compositions of sediments and sludges necessitated some minor modifications to the sludge methods in order to apply them to sediments. Sediments typically contain higher solids contents than sludges, and the suspended solids have a much broader range of densities, typically from near 1.0 g/ml for biogenic materials to 2.6 g/ml for siliceous minerals. In addition, sediments generally have a lower total organic carbon level compared to sludges. The effects of these differences generally influenced only the purging and extraction procedures.

SAMPLE COLLECTION AND CHARACTERIZATION

Sediment samples were collected from three points along the Blue River in Kansas City, Missouri. Samples were collected with a Ponar dredge from bridges crossing the river at Grandview Road and at 15th Street. Samples were collected with a shovel from the east bank of the river 15 to 20 m north of the bridge at Blue Parkway (Highway M-350). The Grandview Road site is 300 to 400 m downstream from a large electrical component manufacturing plant. The Blue Parkway and 15th Street sampling sites are just downstream of asphalting and creosoting plants, respectively. All samples were dark-colored and had strong odors. The samples were stored at 4°C immediately upon arrival at MRI. The solids contents of each sample were determined gravimetrically by drying 1- to 3-g aliquots at 110°C overnight. Total organic carbon was determined in aliquots of each sample by oxidation to carbon dioxide and infrared detection. The solids and total organic carbon contents for each sediment sample are listed in Table 56.

EVALUATION OF SEDIMENT SPIKING

Since the high solids content of sediments may hinder mixing of an organic spiking solution with sediment, the mixing times required to achieve homogeneous spike distribution in aliquots of Blue River sediment were investigated. This study was simplified by using radiolabeled compounds representative of the three analytical classes. The compounds used were ^{14}C-phenol and ^{14}C-2,5-dichlorophenol to represent acidic extractables, and ^{14}C-fluorene to represent base/neutral extractables.

TABLE 56. BLUE RIVER SEDIMENT SAMPLES COLLECTED FOR EVALUATING THE PRELIMINARY POTW PROTOCOL

Sampling location	Solids content (%)	Total organic carbon (mg/g dry weight)
Grandview Road Bridge	65	4.4
Blue Parkway	48	11.0
15th Street Bridge	39	13.0

Experimental

Aliquots of sediments from the 15th Street Bridge site (approximately 500 g) were placed in 500-ml (nominally 16-oz) glass screw-cap jars. The contents of the jars were spiked with 1.0 ml of an acetone solution containing etier ^{14}C-phenol at 10.0 µCi/ml, ^{14}C-2,5-dichlorophenol at 9.5 µCi/ml, or ^{14}C-fluorene at 5.5 µCi/ml. The jars were sealed with TFE-lined caps and were tumbled. Aliquots were removed at several time periods from 0 to 104 h. At each time period three 1-g aliquots were removed from different locations in the jars. These aliquots were extracted with 6.0 ml of toluene with a vortex mixer and centrifuged for 10 min at 3,400 rpm. A 1.0-ml portion of each extract was assayed by liquid scintillation counting. Determinations were made with a Packard Model 2420 Tri-Carb Liquid Scintillation Spectrometer using a scintillation cocktail containing 0.47% PPO (2,5-diphenyl oxazole) as primary scintillator and 0.006% POPOP (p-bis[2-(5-phenyloxazole)]-benzene) as secondary scintillator in toluene. All extracts were counted for 2 or 4 min and the counting efficiency was determined by an automatic external standard ratio method. The dry weights of the sediment aliquots assayed were determined after drying overnight at 110°C.

Similar experiments were conducted using ^{14}C-benzene. The principal differences were that larger sediment aliquots (approximately 630 g) were spiked and the jars were topped off with a small volume of water each time they were sealed to remaintain zero headspace during mixing. The samples were spiked with 1.0 ml of a 10 µCi/ml solution of ^{14}C-benzene in methanol.

Results and Discussion

The results of long-term equilibration studies for fluorene, phenol, and 2,5-dichlorophenol was summarized in Figures 69 to 71. The ranges of ^{14}C contents of aliquots sampled at each time indicate that fairly uniform distribution for each compound was achieved within 8 h after spiking. The equilibrium levels observed for phenol, 2,5-dichlorophenol, and fluorene at 8 h were 80, 85, and 100%, respectively, of the levels spiked. Fluorene levels in the spiked sediment remained fairly constant and uniform throughout the 104-h experiment. Although the mean phenol levels remained fairly constant and uniform through 48 h, the range of phenol in aliquots taken at 104 h was 61% of the mean. Levels of 2,5-dichlorophenol remained uniform throughout the experiment but decreased to about half of the initial equilibration level. The loss may be attributable to degradation of the analyte. Hence, it may be advisable to extract spiked sediment aliquots during the period of 10 to 48 h following fortification.

The results of the spike equilibration study for benzene are summarized in Figure 72. Uniform distribution of the spike was achieved after 6 h and the equilibrium level remained fairly constant following equilibration. The equilibrium level achieved was 35% of the theoretical spike level. Losses are likely attributable to volatilization of the spiked benzene during spiking or sample handling immediately following spiking.

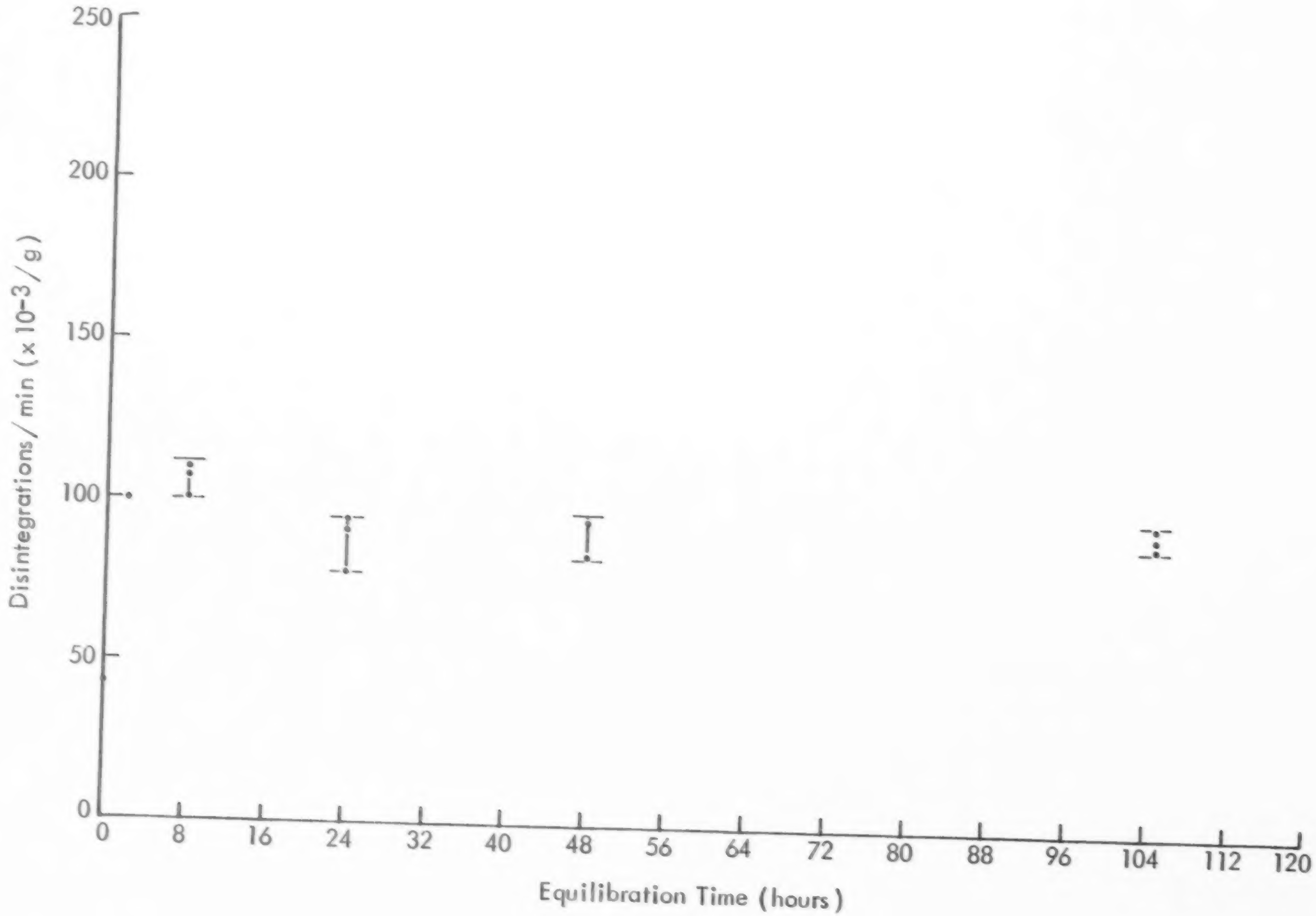

Figure 69. Results of equilibration of ^{14}C-fluorene spiked in sediment.

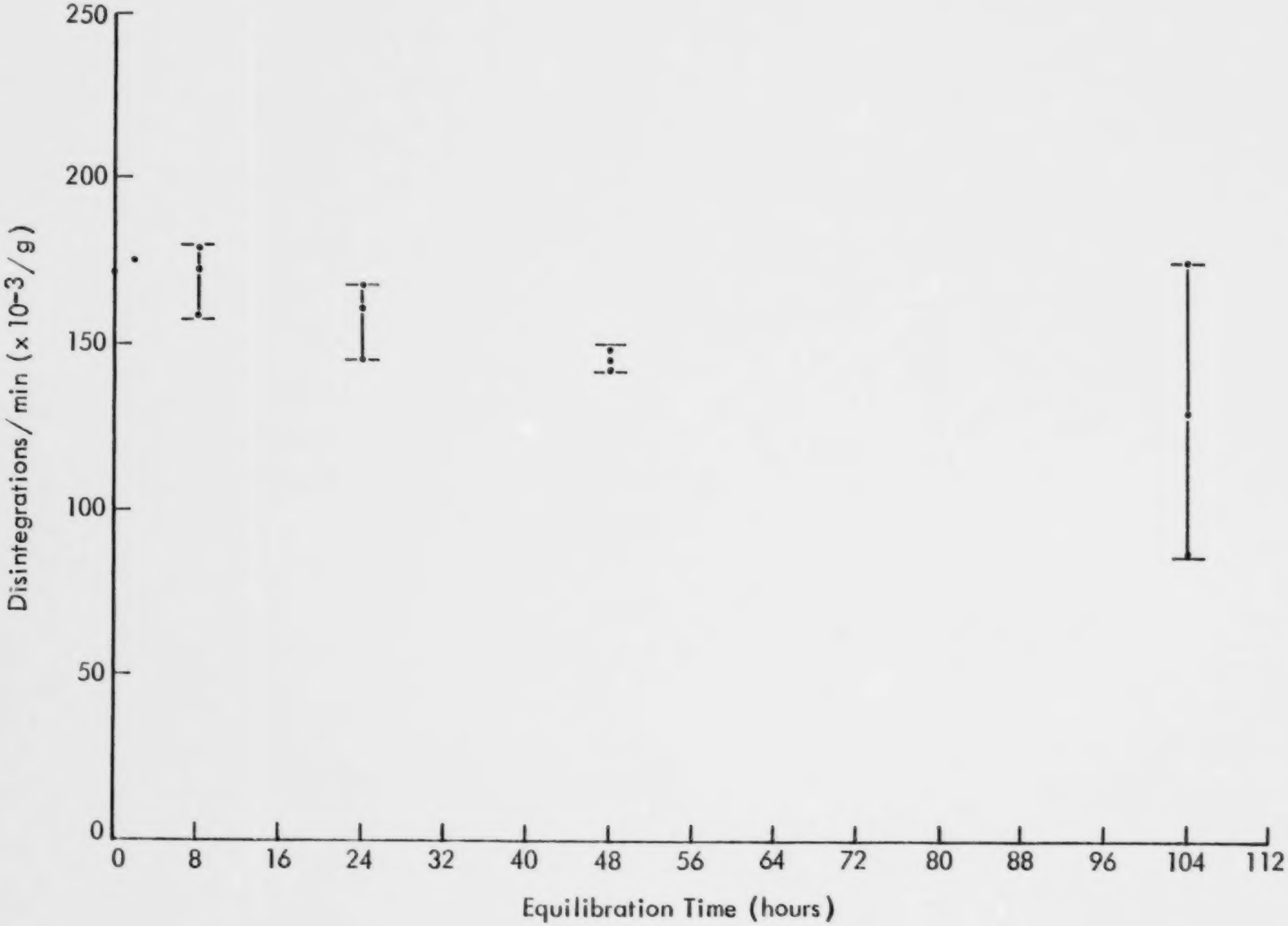

Figure 70. Results of equilibration of ^{14}C-phenol spiked in sediment.

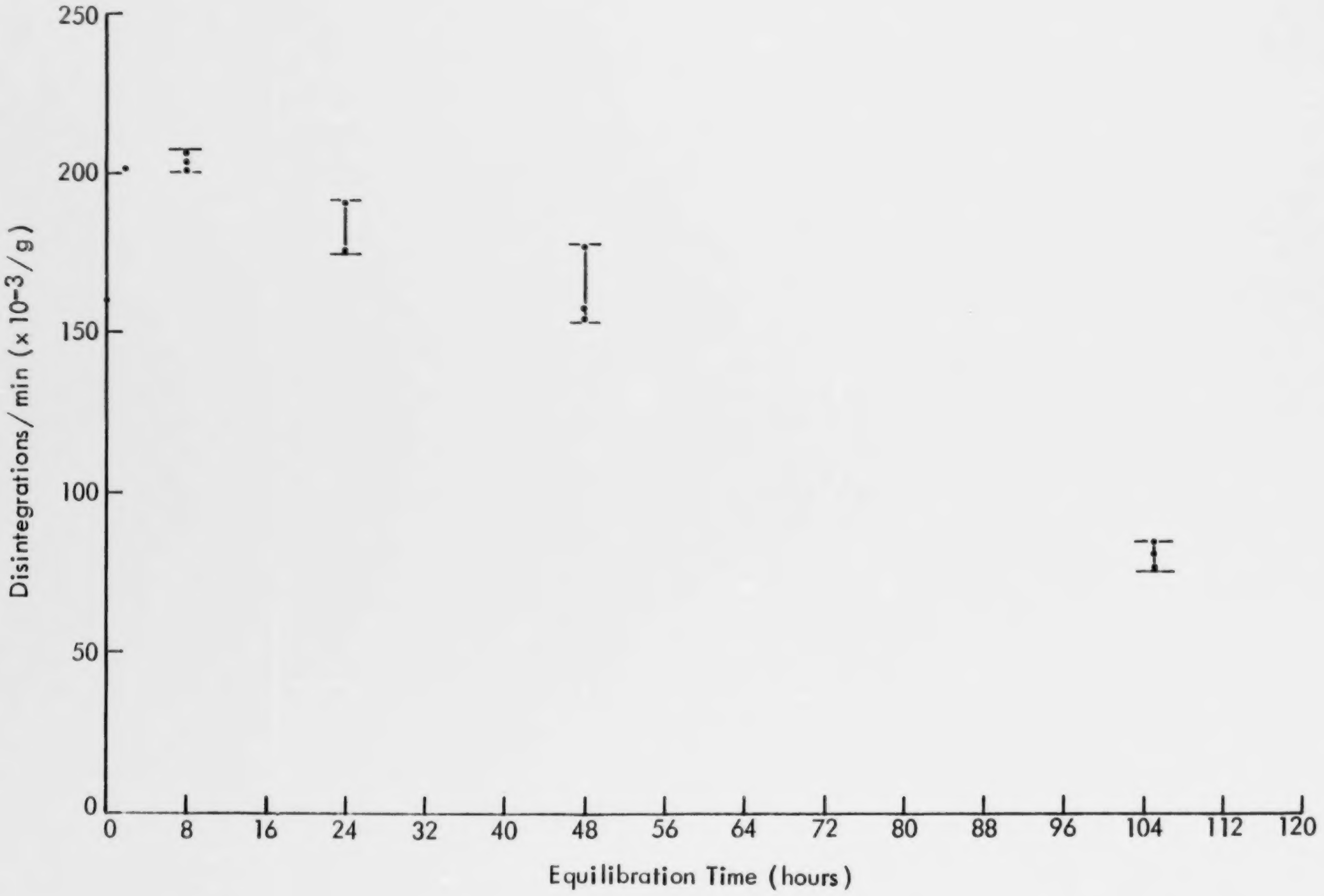

Figure 71. Results of equilibration of ^{14}C-2,5-dichlorophenol spiked in sediment.

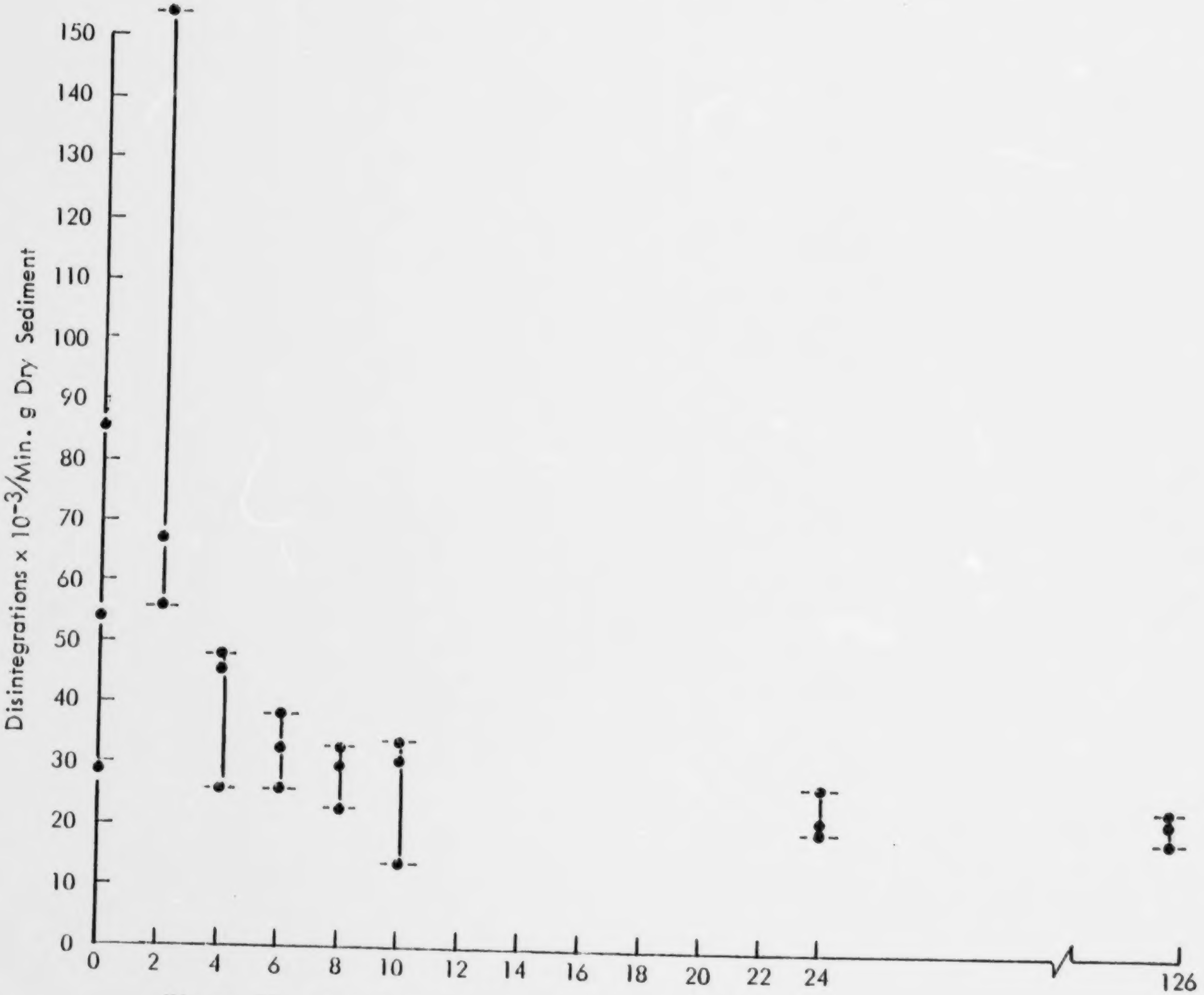

Figure 72. Results of equilibration of ^{14}C-benzene spiked in sediment.

ANALYSIS OF PURGEABLE COMPOUNDS

Since the lower total organic carbon content of sediments relative to sludges may influence purging efficiencies, a preliminary investigation of purging from various concentrations of sediment in suspension was conducted. Recoveries were then determined for compounds spiked into sediment and analyzed using the optimum suspension concentration.

Evaluation of the Effect of Solids Dilution on Purging

Experimental--

Suspensions containing 10, 30, 50, and 80% wet sediment (by weight) were prepared with sediment from the 15th Street site. Ten-milliliter aliquots of each suspension were spiked with 250 ng each of the purgeable spiking compounds and analyzed by the purge-trap GC/MS method described in the preliminary POTW sludge protocol. No foaming of the suspensions was observed.

Results and Discussion--

The quantities of the purgeable compounds determined in the sediment suspensions are shown in Table 57. The quantities are also plotted versus the sediment concentration in the suspensions in Figure 73. Levels for toluene were not plotted, nor were the anomalously low levels observed in the 50% suspensions. From these results, it is apparent that chloroform, 1,1-dichloroethene, 1,2-dichloroethane, dichloromethane, and toluene were present in the unspiked sediment at significant concentrations. The purging efficiencies for the various compounds appeared to be affected differently. The levels of chlorobenzene, ethylbenzene, trichloroethene, and 1,1,1-trichloroethane were decreased slightly at higher sediment concentrations. The purging efficiency for 1,1,2,2-tetrachloroethane was much lower in the 80% suspensions. Purging efficiencies appeared to be good for all compounds in the 30% suspension. Further dilution did not provide markedly higher recoveries but did decrease the method detection limit. Hence, 30% sediment suspension was selected for subsequent purging studies.

Determination of Recoveries from Spiked Sediment

Experimental--

Five aliquots for each Blue River sediment sample were placed in 40-ml vials. Two stainless steel balls were added to each vial, and the vials were sealed with no headspace. Three vials for each sample were spiked with 5.0 µl of a solution containing the purgeable spiking compounds to achieve spike concentrations of 55 to 60 ng/g wet sediment. The vials were tumbled overnight at 4°C to allow equilibration of the spike. A single 3-g aliquot from each vial was diluted to 10 ml and analyzed by the purge-trap GC/MS procedures described in the preliminary sludge protocol. Duplicate unspiked aliquots and triplicate spiked aliquots were analyzed for each sediment sample.

Results and Discussion--

The results of the recovery experiments are shown in Table 58. The recoveries observed were much higher for the Blue Parkway and 15th Street samples. The compounds that were found at significant concentrations in unspiked 15th Street samples in the preceding experiment were likely lost during storage.

TABLE 57. RESULTS OF ANALYSES OF VARIOUS SEDIMENT-WATER SUSPENSIONS (10-80% SEDIMENT) BY PURGE-TRAP GC/MS FOLLOWING FORTIFICATION WITH 250 ng EACH OF SELECTED COMPOUNDS

Compound	Weight of compounds observed (ng)			
	10%	30%	50%	80%
Benzene	201	262	141	221
1,1,2,2-Tetrachloroethane	196	144	34	1
Chloroform	215	319	253	452
1,1-Dichloroethene	264	281	403	607
1,2-Dichloroethane	233	343	371	614
Dichloromethane	273	406	429	472
Trichloroethene	243	178	107	149
1,1,1-Trichloroethane	211	192	99	118
Chlorobenzene	213	185	111	164
Toluene	1,390	1,670	1,250	1,900
Ethylbenzene	197	176	95	156

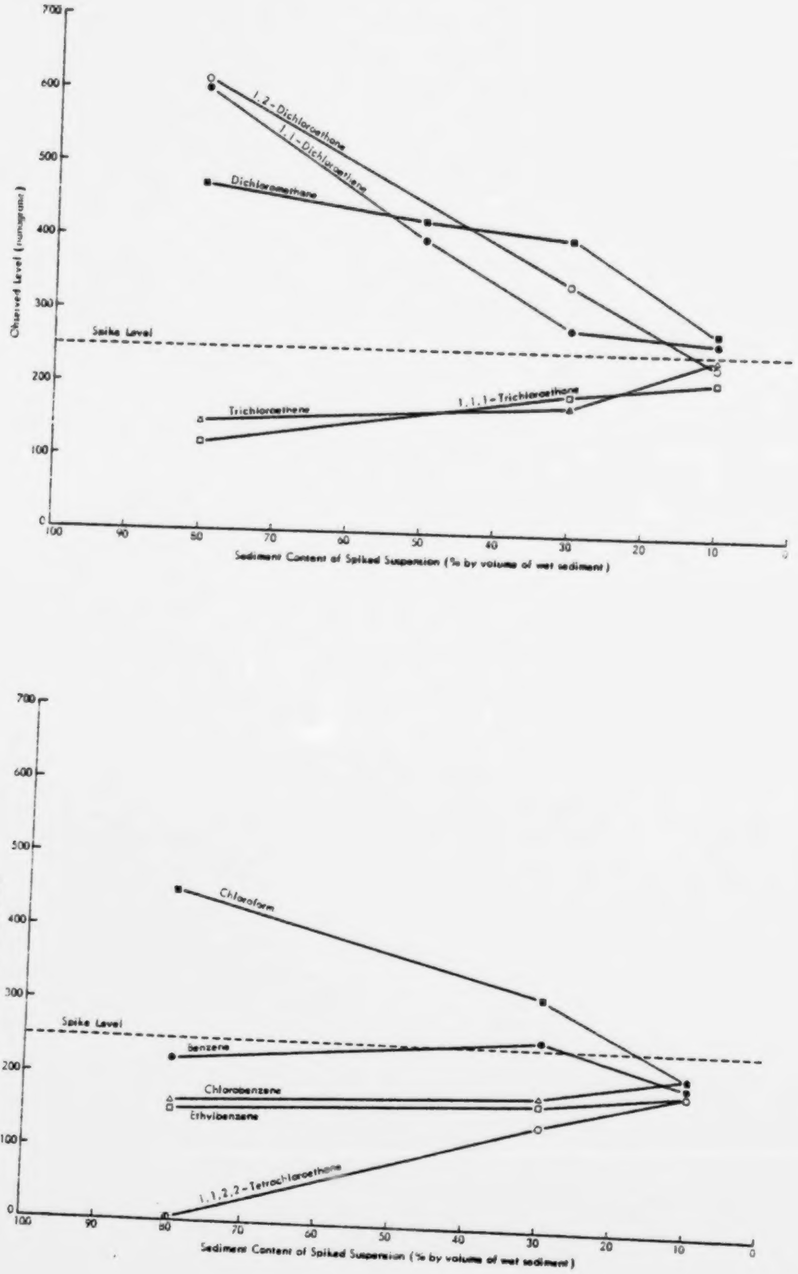

Figure 73. Results of analyses of sediment-water suspensions by purge-trap GC/MS following fortification with 250 ng each of selected compounds.

TABLE 58. RESULTS OF EVALUATION OF POTW SLUDGE PURGEABLES METHOD FOR SPIKED SEDIMENTS

Compound	Spike level (ng/g)	Grandview Road		Blue Parkway		15th Street	
		Unspiked level (ng/g)	Spike recovery (%)	Unspiked level (ng/g)	Spike recovery (%)	Unspiked level (ng/g)	Spike recovery (%)
Benzene[a]	55	ND[b]	61 ± 26[c]	ND	86 ± 14	ND	187 ± 42
Carbon tetrachloride	55	ND	0	ND	0	ND	131 ± 136
Chlorobenzene[a]	55	ND	26 ± 26	ND	60 ± 8	ND	155 ± 42
Chloroform	55	ND	5 ± 8	ND	152 ± 42	ND	57 ± 69
1,2-Dichloroethane	55	ND	42 ± 14	ND	111 ± 39	ND	162 ± 94
Vinylidene chloride	55	ND	36 ± 11	ND	109 ± 8	ND	165 ± 75
Ethylbenzene[a]	55	ND	21 ± 24	ND	123 ± 20	ND	108 ± 4
Tetrachloroethene	55	ND	22 ± 30	ND	148 ± 28	ND	122 ± 13
1,1,1-Trichloroethane	55	ND	6 ± 10	ND	81 ± 2	ND	101 ± 90
Trichloroethylene	55	ND	23 ± 18	ND	101 ± 14	ND	138 ± 43
Vinyl chloride	55	ND	46 ± 1	ND	132 ± 29	ND	119 ± 37

[a] Because of saturation of primary ions, secondary ions were used for quantitation.

[b] ND = not detected.

[c] Mean recovery ± standard deviation of three replicates.

Since the samples were collected for spike recovery experiments and not for accurate characterization of ambient concentrations of purgeables, they were stored without concern for maintaining zero headspace. The recoveries determined for triplicate spiked samples were quite variable for many compounds. Part of the variability likely reflects the lack of homogeneity achieved in the spiked aliquots.

The results of this evaluation indicated that the sludge purge-trap GC/MS methods may be successfully applied to sediment analysis. As in the case of sludges, the precision and accuracy of the method may be improved through the use of mechanical mixing of the sediment suspension during purging, i.e., the MRI-designed stirred purge system. However, the abrasive character of sandy sediments may decrease the usable lifetime of the purging equipment.

ANALYSIS OF EXTRACTABLE COMPOUNDS

Determination of Recoveries from Spiked Sediment

Preliminary attempts to extract sediment aliquots with the homogenization/centrifugation method used for sludges indicated that some modification of the procedure was required. The sediment solids were not cleanly separated from the extract by centrifugation because of the wide range of particle densities. However, sediments that had been fractionated by centrifuging and decanting could be homogenized with dichloromethane and centrifuged to cleanly recover the extract. Therefore, the extraction procedure was modified to include this fractionation. The sediment supernatants were extracted separately.

Experimental--

Five hundred gram portions (in 16-oz jars) of Blue River sediment samples were spiked with 300 µg of each of the extractable spiking compounds. Hence, the nominal spike concentrations were 600 ng/g wet sediment. After tumbling overnight at 4°C to allow for equilibration of the spikes, the contents of each jar were equally divided into three portions. The triplicate portions were each subdivided into four 200-ml centrifuge tubes. The aliquots were basified to pH 11 and centrifuged. The supernatants were transferred to 125-ml separatory funnels. Dichloromethane (100 ml) was added to each residue. The content of each tube was homogenized and centrifuged and the extract removed. The aliquots were similarly extracted twice more and the extracts combined. The aqueous supernatants were batch extracted three times with an equal volume of dichloromethane and the extracts combined with the solids extracts. The aqueous supernatant was then distributed equally among the four solids aliquots, and the water-sediment mixtures were adjusted to $pH \leqq 1$. The aliquots were again separated and extracted for acidic compounds in a manner similar to extraction for base/neutral compounds. Acids and base/neutral extracts were cleaned by GPC and analyzed by GC/MS by preliminary POTW sludge protocol procedures. Concentrations of compounds identified were calculated on a dry solids weight basis.

Results and Discussion--

The results of the recovery determinations for compounds spiked into sediments are shown in Table 59. The recoveries observed were generally good for most compounds. The recoveries for the phenolic compounds were particularly good and reproducible, except for 2,4-dimethylphenol. Many of the B/N

TABLE 59. RESULTS OF EVALUATION OF MODIFIED POTW SLUDGE EXTRACTABLES METHOD FOR SPIKED SEDIMENTS

Compound	Spike level (ng/g)	Grandview Road		Blue Parkway		15th Street	
		Unspiked level (ng/g)	Spike recovery (%)	Unspiked level (ng/g)	Spike recovery (%)	Unspiked level (ng/g)	Spike recovery (%)
1,4-Dichlorobenzene	629	3	47 ± 9[a]	2	37 ± 2	17	50 ± 7
Hexachloroethane	632	ND[b]	0	ND	0	ND	0
Bis(2-chloroisopropyl)ether	656	ND	c	ND	c	ND	51 ± 2
Bis(2-chloroethyl)ether	599	ND	51 ± 16	ND	33 ± 5	ND	46 ± 4
Acenaphthylene	634	4	58 ± 14	5	57 ± 4	ND	86 ± 11
2,6-Dinitrotoluene	636	ND	0	ND	2 ± 4	ND	0
Fluoranthene	547	390	27 ± 21	360	58 ± 28	1,400	85 ± 28
Benzidine	618	ND	29 ± 14	ND	20 ± 1	ND	22 ± 3
3,3'-Dichlorobenzidine	726	ND	85 ± 27	ND	64 ± 4	ND	70 ± 6
n-Butylbenzylphthalate	714	92	310 ± 100	100	120 ± 110	550	82 ± 3
Bis(2-ethylhexyl)phthalate	670	830	31 ± 29	490	26 ± 4	1,200	d
Benzo[a]pyrene	622	150	45 ± 16	180	68 ± 13	380	76 ± 13
Phenol	674	50	67 ± 6	10	65 ± 2	130	79 ± 10
2,4-Dimethylphenol	694	ND	28 ± 5	ND	38 ± 4	160	52 ± 6
2,4-Dichlorophenol	655	ND	65 ± 10	3	73 ± 4	ND	86 ± 7
Pentachlorophenol	673	ND	86 ± 22	ND	73 ± 13	38	84 ± 4

[a] Mean ± standard deviation for three determinations.

[b] ND = not detected.

[c] This compound was not present in the spiking solution.

[d] Recoveries were not determined for this compound because of high levels in the unspiked sample.

recoveries were somewhat variable. Although benzidine recoveries were low and variable, 3,3'-dichlorobenzidine recoveries were good and fairly reproducible.

In general, the POTW sludge extractables method as modified appeared to provide fairly good results for sediments. However, since separate extraction of supernatants was required, the sediment extraction procedure was even more labor-intensive than sludge extraction. Hence, alternate sediment extraction methods were briefly investigated.

Evaluation of Alternate Extraction Methods

Two alternate procedures were evaluated for sediment extraction by comparing the concentrations determined for neutral extractable compounds in replicate aliquots of unspiked Blue River sediment. The sediment was collected from the 15th Street bridge but was not a replicate of the sample used in the preceding experiments. Extractive steam distillation, described in Section 5, and sequential Soxhlet extraction with a hydrophilic solvent and then a hydrophobic solvent, using methanol then dichloromethane, were compared with the homogenization/centrifugation procedure described in the preceding experiment.

Experimental--

A 175-g aliquot of wet sediment was diluted with 300 ml of glass-distilled water. The sediment-water suspension was extracted for 6 h with 300 ml of dichloromethane using the extractive steam distillation system described in Section 5. The extract was concentrated to 5.0 ml for analysis. A second wet sediment aliquot (84.6 g) was centrifuged and the excess water was decanted. The residue was transferred to a preextracted cellulose thimble measuring 30 mm x 77 mm and extracted with 200 ml of methanol for 8 h. The extract was removed and the sediment extracted an additional 8 h with 200 ml of dichloromethane. The methanol extract, containing 10 to 15 ml of water, was concentrated to approximately 25 ml in a Kuderna-Danish evaporator and extracted with three 25-ml portions of dichloromethane. This extract and the dichloromethane sediment extract were independently concentrated to 5.0 ml for analysis. A third wet sediment aliquot of 160 g was extracted at ambient pH by the homogenization/centrifugation procedure described in the preceding experiment. The homogenization extract was cleaned by GPC and the cleaned extract was concentrated to 5.0 ml for analysis. All extracts were screened by GC/FID and then analyzed for all neutral organic priority pollutants by GC/MS using the preliminary POTW sludge protocol procedures.

Results and Discussion--

The concentrations determined for neutral organic priority pollutants in the sediment aliquots extracted by steam distillation, Soxhlet, and homogenization/centrifugation procedures are shown in Table 60. GC/FID chromatograms for each extract are shown in Figures 74 to 77. The GC/FID chromatograms illustrate that the rigorous homogenization/centrifugation procedure, even with GPC cleanup, produces extracts with higher levels of unresolved coextractants than steam distillation or Soxhlet extraction. However, the highest concentrations of the analytes were observed in the Soxhlet extracts. Further development of sediment extraction procedures should be focused on techniques which are more selective and efficient than homogenization/centrifugation.

TABLE 60. ORGANIC PRIORITY POLLUTANTS IDENTIFIED IN BLUE RIVER SEDIMENT BY SOXHLET EXTRACTION, STEAM DISTILLATION, AND HOMOGENIZATION

Compound identified	Concentration (ng/g dry sediment)				
	Soxhlet			Steam distillation	Homogenization
	CH_3OH	CH_2Cl_2	Total		
Acenaphthene	48	42	90	87	21
Fluorene	60	40	100	84	24
Phenanthrene/ Anthracene[a]	380	430	810	450	120
Dimethylphthalate	13	2	15	ND[b]	ND
Diethylphthalate	33	11	50	ND	35
Fluoranthene	430	1,200	1,600	470	170
Pyrene	330	900	1,200	370	140
Di-_n_-butylphthalate	47	23	80	48	43
Butylbenzylphthalate	ND	53	53	ND	93
Benzanthracene/ Chrysene[a]	170	780	950	76	76
Bis(2-ethylhexyl)-phthalate	180	90	270	260	130
Benzofluoranthenes[a]	70	500	570	7	44
Benzo[_a_]pyrene	120	900	1,000	ND	88
Indeno[1,2,3-_cd_]pyrene	5	50	56	ND	ND
Dibenz[_a_,_h_]anthracene	ND	23	23	ND	ND
Benzo[_g_,_h_,_i_]perylene	10	92	100	ND	ND

[a] Concentrations represent sums of these compounds which elute simultaneously and have the same major ions for GC/MS.

[b] ND = not detected.

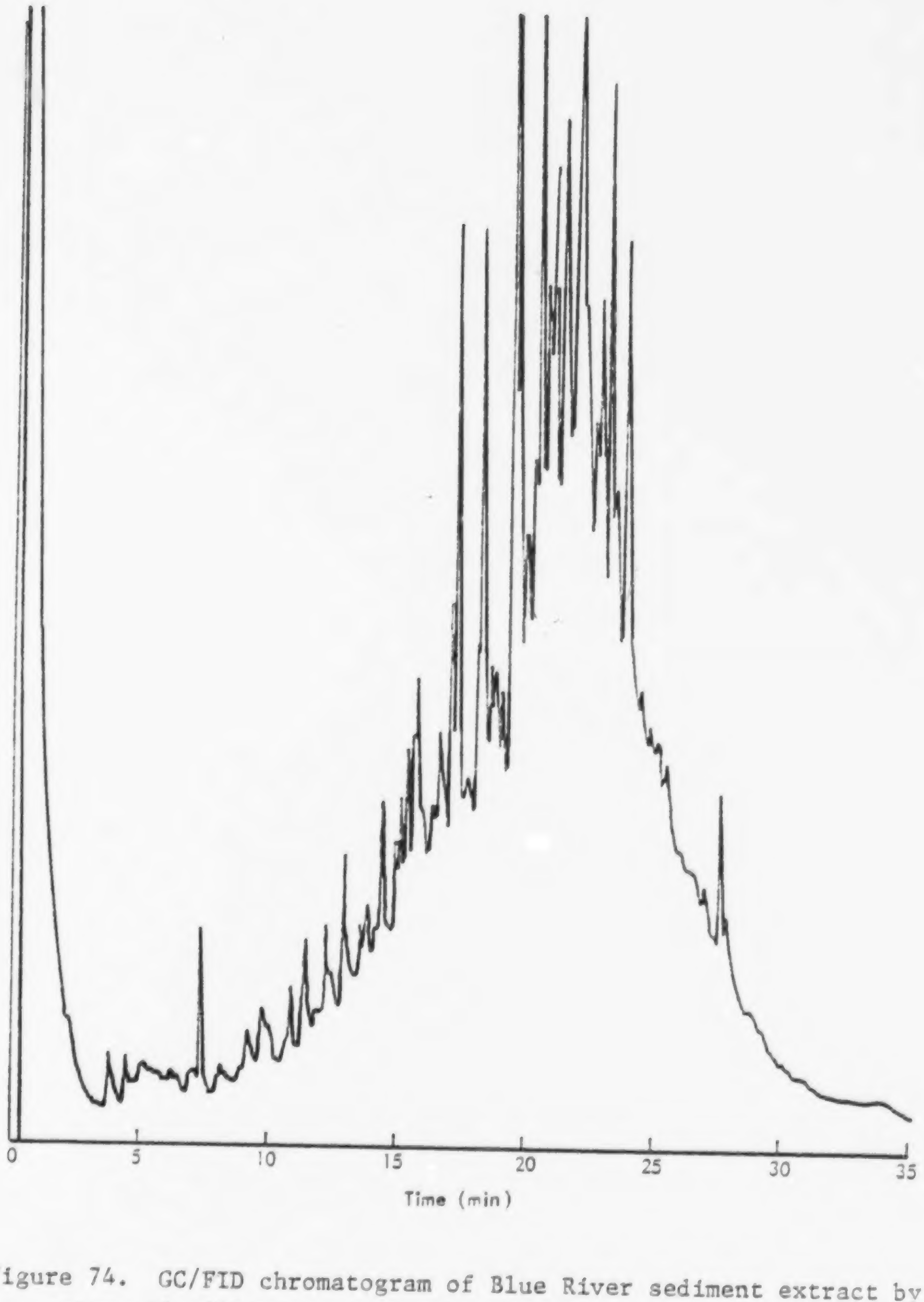

Figure 74. GC/FID chromatogram of Blue River sediment extract by steam distillation-continuous extraction - no cleanup.

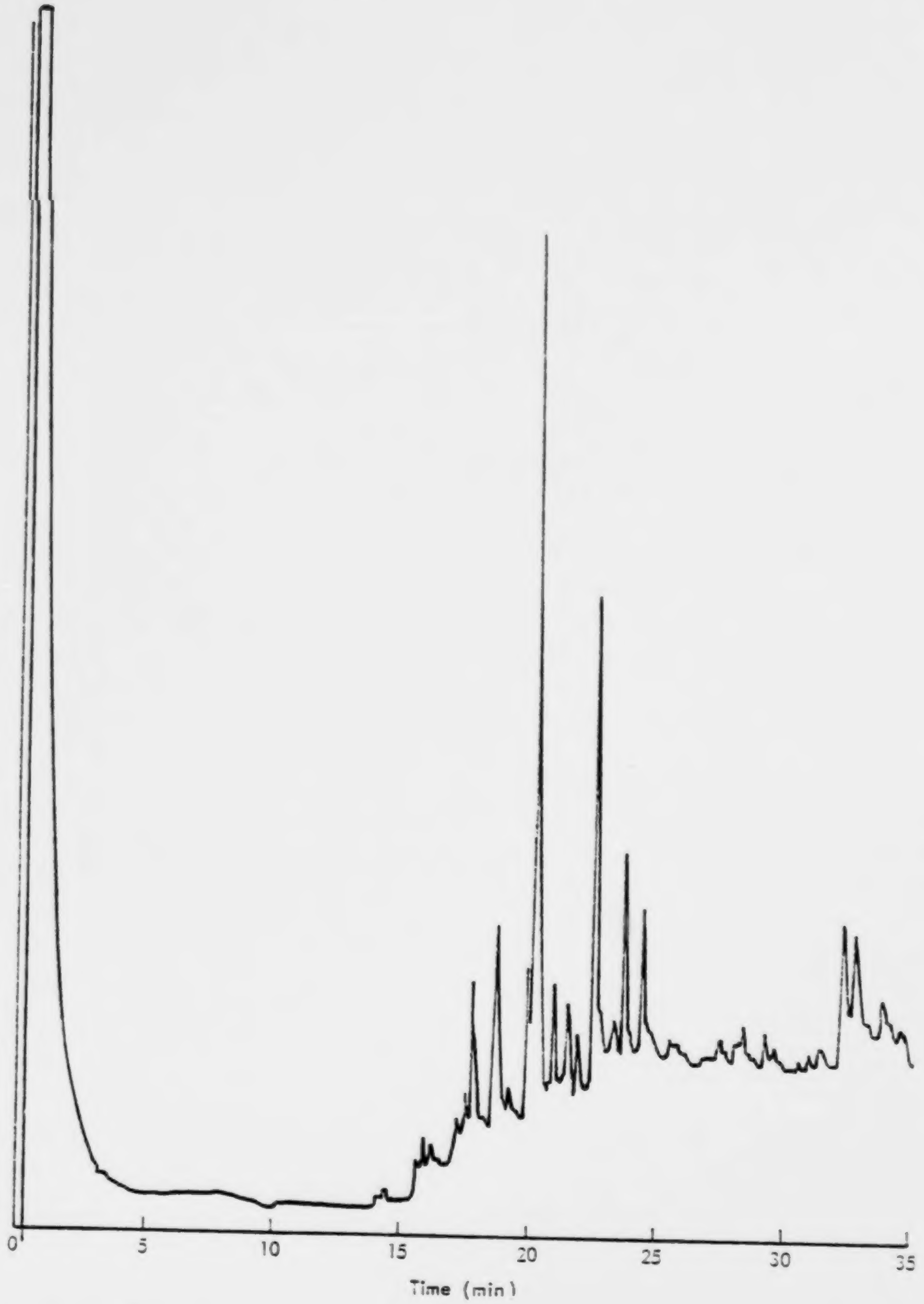

Figure 75. GC/FID chromatogram of Blue River sediment extract by Soxhlet with methanol - no cleanup.

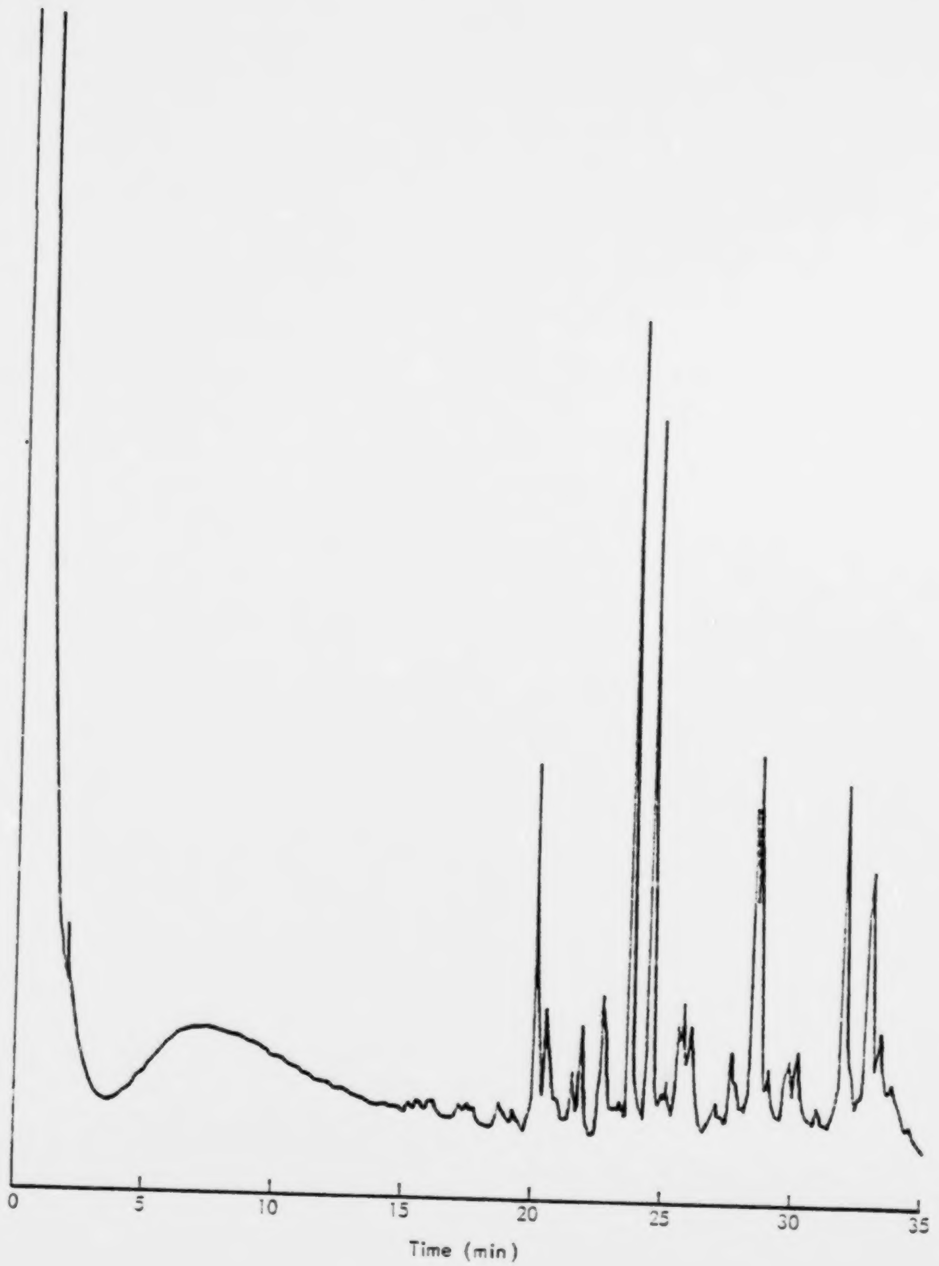

Figure 76. GC/FID chromatogram of Blue River sediment extract by Soxhlet with dichloromethane (preextracted with methanol) - no cleanup.

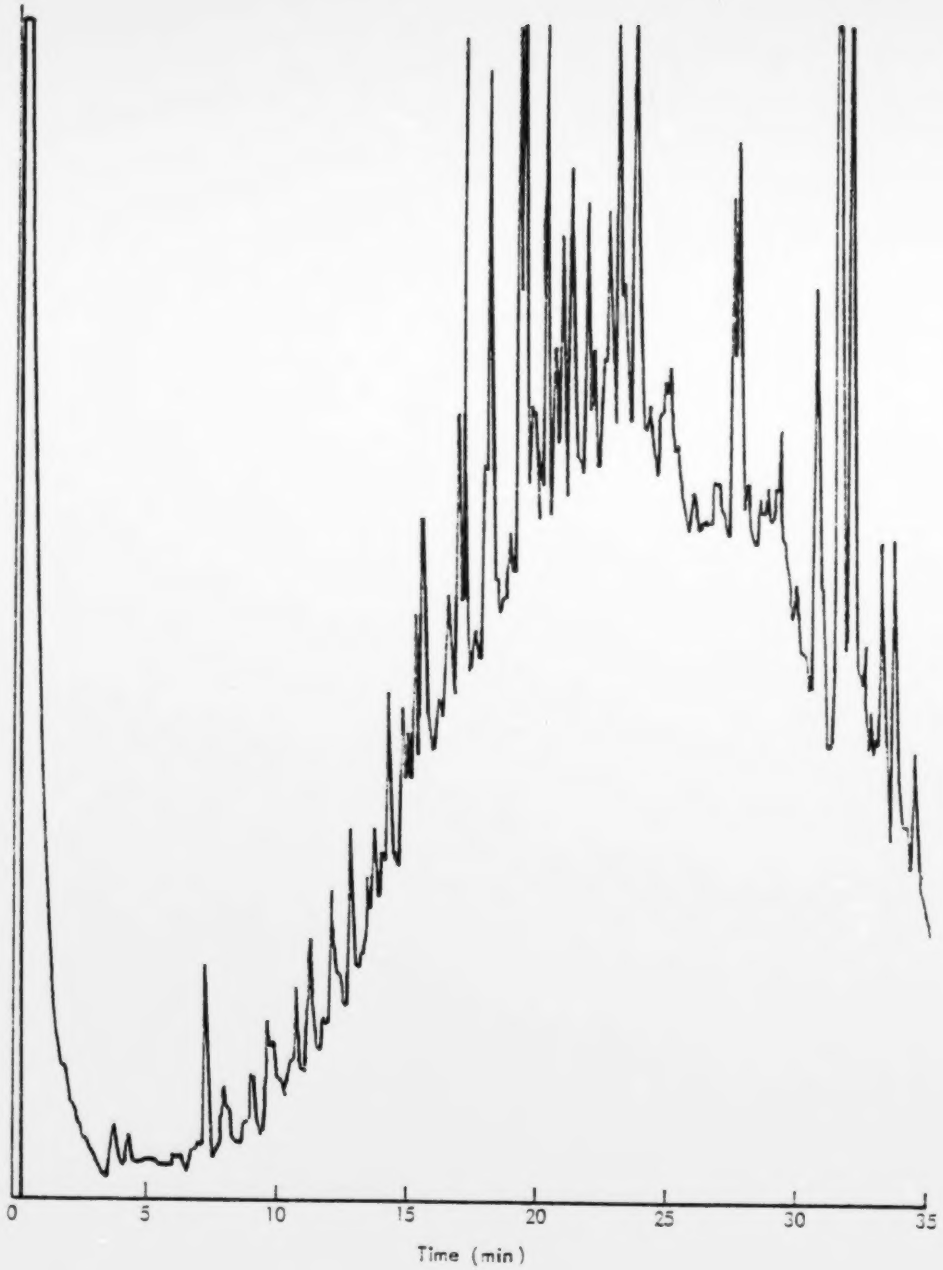

Figure 77. GC/FID chromatogram of Blue River sediment extract by homogenization following cleanup by GPC.

SECTION 7

DETERMINATION OF THE PHASE DISTRIBUTION OF SELECTED COMPOUNDS IN 1% PRIMARY SLUDGE

The distributions of contaminants between solution and solids in wastewaters and sludges are key factors in influencing the transport of those contaminants within the wastewater treatment system. In particular, compounds with low aqueous solubilities may strongly associate with solids. Hence, solids wasting from a treatment system may be the primary emission mode; i.e., solids removal from the wastewater may also provide efficient removal of hydrophobic contaminants. The objective of the experiments described in this section was to determine the distributions of selected purgeable and extractable compounds spiked in two samples of 1% primary POTW sludge at two or more levels. The development of analytical methods for sludges, described in the preceding sections, facilitated the experimental determination of phase distributions.

The phase distributions determined for each compound were expressed as follows:

$$K_{\text{distribution}} = \frac{C_{\text{solids}}}{C_{\text{supernatant}}}$$

where: $K_{\text{distribution}}$ is the phase distribution coefficient

C_{solids} is the concentration of the analyte in the suspended solids (ng/g)

$C_{\text{supernatant}}$ is the concentration of the analyte in the sludge supernatant (μg/liter)

The target spiking levels for the phase distribution experiments were 100 and 1,000 times the detection limit of the analytical method. However, the aqueous solubility for each compound was a primary consideration in determining the actual spiking levels. The spiking compounds may be found in sludges at concentrations in excess of their aqueous solubilities because a fraction is associated with the suspended solids. Hence, sludges can be spiked with many compounds at levels exceeding aqueous solubilities for the purpose of determining analytical recoveries with some measure of confidence. However, more accurate phase distribution information will result from experiments where the suspended solids are exposed to the spiked compounds in solution. That is, spiking levels should be equal to or less than the aqueous solubility for each compound.

The solubilities of the purgeable spiking compounds in water are listed in Table 61. The solubilities for all compounds except vinyl chloride are greater than 150 mg/liter. Assuming a conservative analytical detection limit of 5 µg/liter, all compounds except vinyl chloride could be spiked at 1,000 times the detection limit without exceeding their aqueous solubilities.

The aqueous solubilities for the extractable spiking compounds are listed in Table 62. The extractable compounds were divided into four groups based on solubility and analytical class to allow convenient spiking and analysis. The first three groups are base/neutral compounds selected according to solubilities and the fourth group contains the phenolic compounds. Only four compounds from the more soluble Group I B/Ns and three phenols from Group IV have solubilities exceeding 1,000 times a conservative detection limit of 250 µg/liter. The spike levels for the phase distribution experiments were selected to be lower than the solubility of the least soluble compound in each group. The very low aqueous solubility of benzo[a]pyrene, the only Group III compound, was too low to allow either spiking at soluble levels for analysis of fractions by GC/MS methods. Hence, phase distributions were not determined for benzo[a]pyrene.

The sludges used in the phase distribution experiments were the Platte County, Kansas City, Kansas, and Blue River primary POTW sludges described in Table 18. Experiments for purgeables were conducted with the Platte County and Kansas City, Kansas, sludges. Experiments for extractables used the Platte County and Blue River sludges. Sludge aliquots were diluted to 1% suspended solids with purgeables-free water prior to spiking with the purgeable compounds in methanol. Since the solubilities of many of the extractable compounds are much lower than the purgeable compounds, sludge aliquots used in the phase distribution studies for extractable compounds were diluted to 1% suspended solids with a solution of the spiking compounds in glass-distilled water. Spiking was done in this manner to ensure that the less soluble compounds would be dissolved before being exposed to the solids.

PURGEABLE COMPOUNDS

Although recoveries had been determined for selected purgeable compounds spiked into primary sludge from the Platte County and Kansas City, Kansas, POTWs (see Section 4), recoveries were also measured for the same compounds spiked into sludge aliquots diluted to 1% suspended solids to provide an indication of the precision and accuracy of the subsequent distribution experiments.

Determination of Recoveries from Spiked 1% Sludge

Experimental--

Aliquots of primary sludge were diluted to 1% suspended solids with purgeables-free water, spiked, and analyzed as described in the Method Appendix. Recoveries were determined in triplicate.

TABLE 61. WATER SOLUBILITIES OF PURGEABLE SPIKING COMPOUNDS

Compound	Water solubility[a] at 20°C (µg/L)
Benzene	1,800,000 (25°C)
Carbon tetrachloride	785,000
Chloroform	8,200,000
1,1-Dichloroethene	400,000
Tetrachloroethene	150,000
Vinyl chloride	1,100 (25°C)
1,2-Dichloroethane	3,690,000
Trichloroethene	1,100,000
1,1,1-Trichloroethane	4,400,000
Chlorobenzene	500,000
Ethylbenzene	152,000

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[a] U.S. Environmental Protection Agency. Water-Related Environmental Fate of 129 Priority Pollutants, Vol. II. EPA-440/4-79-029b, December 1979.

TABLE 62. WATER SOLUBILITIES OF THE EXTRACTABLE SPIKING COMPOUNDS

Compound	Water solubility at 20-25°C (μg/L)	Literature reference
Group I		
1,4-Dichlorobenzene	79,000	a
Hexachloroethane	50,000	b
Bis(2-chloroisopropyl)ether	1,700,000	b
Bis(2-chloroethyl)ether	10,200,000	c
2,6-Dinitrotoluene	300,000	d
Benzidine	400,000	e
3,3'-Dichlorobenzidine	NA	-
Group II		
Acenaphthylene	3,930	c
Fluoranthene	300	f
n-Butylbenzylphthalate	2,900	c
Bis(2-ethylhexyl)phthalate	400	g
Group III		
Benzo[a]pyrene	4	f
Group IV		
Phenol	93,000,000	c
2,4-Dimethylphenol	17,000,000	c
2,4-Dichlorophenol	4,500,000	d
Pentachlorophenol	14,000	c

a Chion, C. T. et al. Environ. Sci. Technol. 11:475 (1977).

b Kirk-Othmer Encyclopedia of Chemical Technology, 2nd edition, John Wiley and Sons, 1979.

c U.S. Environmental Protection Agency, Water-Related Environmental Fate of 129 Priority Pollutants, Vol. II. EPA-440/4-79-029B, December 1979.

d Lange's Handbook of Chemistry, 11th edition, McGraw-Hill, 1973.

e Merck Index, 9th edition, M. Windholz (Ed.), Merck & Co., 1976.

f Mackay, D. and W. Y. Shiu, J. Chem. Eng. Data 22:399 (1977).

g Patty, F. A. Industrial Hygiene and Toxicology, Vol. 2, Science Publishers, 1978, p. 1900.

NA = not available.

Results and Discussion--

The results of the recovery determinations are shown in Table 63. Recoveries for all compounds except carbon tetrachloride were within the range of 75 to 140% with good reproducibility. The concentrations of the spiking compounds in the unspiked, diluted sludge were all at or near the detection limit.

Determination of Phase Distributions

Experimental--

Diluted sludge (1% suspended solids) was poured into 200-ml screw-cap centrifuge tubes containing a magnetic stirring bar. The samples were spiked with the purgeable spiking compounds in 10 to 100 μl of methanol and sealed with no headspace with TFE-lined lids. The spiked samples were stirred for 1 min and were allowed to equilibrate at 4°C overnight with tumbling. The phases were separated by centrifuging the bottles at 2,500 rpm for 30 min. The centrifuged aliquots were allowed to cool at 4°C before gently decanting the supernatant. Aliquots of the supernatant were stored in 40-ml vials with no headspace prior to analysis. Immediately following removal of the supernatants, the centrifuge bottles were filled with purgeables-free water and resealed with zero headspace. The reconstituted sludge solids were hand-shaken 1 min and aliquots were removed for analysis. Triplicate aliquots of supernatants and reconstituted solids were analyzed for each spiked sample by the purge-trap GC/MS procedure described in the Method Appendix. The concentrations determined for the supernatants and the corresponding reconstituted solids (dry basis) were used to calculate the phase distribution coefficients for each sludge sample.

Results and Discussion--

The results of the phase distribution determinations are shown in Table 64. The coefficients observed range from less than 10 for vinyl chloride and 1,2-dichloroethane to more than 200 for tetrachloroethene and ethylbenzene. The coefficients were higher for all compounds in the Kansas City, Kansas, sludge. No clear relationships with concentration were apparent in either sludge. The coefficient determinations for each spike level were very reproducible.

EXTRACTABLE COMPOUNDS

In order to provide an indication of the precision and accuracy of the subsequent phase distribution experiments, recoveries were determined for the selected extractable compounds spiked into sludge supernatants and solids from the diluted Platte County and Blue River POTW sludges. In addition, the time required for spikes to achieve equilibrium distribution between supernatant and solids was investigated.

TABLE 63. RECOVERIES FOR PURGEABLE COMPOUNDS SPIKED INTO PRIMARY POTW SLUDGE DILUTED TO 1% SOLIDS

Compound	Spike level (μg/L)	Platte County POTW recovery (%)	Kansas City, Kansas POTW recovery (%)
Benzene	56	93 ± 6[a]	100 ± 3
	560[b]	100 ± 15	120 ± 7
Carbon tetrachloride	539	62 ± 40	62 ± 30
	5,390[b]	31 ± 2	30 ± 11
Chloroform	101	100 ± 7	120 ± 1
	1,010[b]	130 ± 20	99 ± 6
1,1-Dichloroethene	271	77 ± 5	96 ± 2
	2,710[b]	97 ± 15	97 ± 2
Tetrachloroethene	163	78 ± 4	110 ± 10
	1,630[b]	110 ± 6	84 ± 24
Vinyl chloride	170	78 ± 1	90 (4)[c]
	1,700[b]	86 ± 6	100 ± 3
1,2-Dichloroethane	274	98 ± 3	92 ± 4
	2,740[b]	110 ± 4	100 ± 3
Trichloroethene	108	76 ± 12	92 ± 5
	1,080[b]	110 ± 2	86 ± 8
1,1,1-Trichloroethane	866	120 ± 4	140 ± 5
	8,600[b]	130 ± 3	140 ± 19
Chlorobenzene	108	82 ± 7	91 ± 1
	1,080[b]	110 ± 2	94 ± 15
Ethylbenzene	268	79 ± 1	100 ± 3
	2,680[b]	110 ± 2	93 ± 3

[a] Mean ± standard deviation for three determinations.

[b] Analyzed from a 2.0-ml aliquot diluted to 10 ml prior to purging.

[c] Mean (average deviation) for two determinations.

TABLE 64. DISTRIBUTION COEFFICIENTS DETERMINED FOR PURGEABLE COMPOUNDS SPIKED INTO PRIMARY POTW SLUDGE

Compound	Spike level (μg/L)	$K_{distribution}$[a] Platte County POTW	Kansas City, Kansas POTW
Benzene	56	11 ± 1[b]	28 ± 3
	560	23 ± 2	24 ± 5
Carbon tetrachloride	539	34 (10)[c]	76.2 (6)
	5,390	20 ± 4	43 ± 19
Chloroform	101	14 (0.2)	15 ± 1
	1,010	13 (0.8)	17 ± 3
1,1-Dichloroethene	271	6.9 ± 2	23 ± 3
	2,710	48 ± 31	20 ± 3
Tetrachloroethene	163	160 ± 27	380 ± 39
	1,630	260 ± 21	290 ± 100
Vinyl chloride	170	d	6.6 ± 0.4
	1,700	4.4 ± 0.8	3.4 ± 0.3
1,2-Dichloroethane	274	1.7 ± 0.7	7.1 ± 0.5
	2,740	4.5 ± 0.6	2.8 ± 0.3
Trichloroethene	108	40 ± 9	60 ± 6
	1,080	44 ± 3	69 ± 20
1,1,1-Trichloroethane	866	41 ± 4	80 ± 4
	8,600	45 ± 2	61 ± 10
Chlorobenzene	108	53 ± 4	110 ± 14
	1,080	100 ± 13	110 ± 32
Ethylbenzene	268	110 ± 2	230 ± 10
	2,680	190 ± 23	240 ± 84

[a] $$K_{distribution} = \frac{\text{concentration of analyte in solids (ng/g)}}{\text{concentration of analyte in supernatant (ng/ml)}}.$$

[b] Mean ± standard deviation for three determinations.

[c] Mean (average deviation) for two determinations.

[d] Determination was not possible because of coeluting interferences.

Determination of Recoveries from Spiked Fractions of 1% Sludge

Experimental--

Three 80-ml aliquots of each sludge diluted to 1% solids were fractionated by centrifuging 30 min at 2,500 rpm and then decanting the supernatants. The supernatants from two aliquots of each sludge were spiked with the Group I and IV compounds at 1,000 µg/liter and the Group II compounds at 300 µg/liter. The sludge residues were reconstituted by diluting to 80 ml with glass-distilled water and were spiked with the Group I, II, and IV at the same levels as the supernatants. The diluted residues were homogenized for 1 min. All supernatants and reconstituted solids were extracted and analyzed by the procedures described in the extractables protocol (Method Appendix) except that no extract cleanup was performed. Analyses were conducted using packed column GC/MS.

Results and Discussion--

The results of the recovery determinations are shown in Table 65. In general, the recoveries observed were good. However, hexachloroethane and 2,6-dinitrotoluene were not recovered from the Blue River sludge supernatants. Benzidine was not recovered from any of the spiked reconstituted solids samples. Hence, the phase distribution results for these compounds are not meaningful.

Determination of Time Required for Equilibrium Distribution of Spikes Between Phases

Experimental--

Sludge aliquots containing 0.80-g solids were diluted to 80 ml in 200-ml centrifuge tubes with glass-distilled water spiked with the extractable spiking compounds in order to achieve concentrations of 5,000 µg/liter for the Group I and IV compounds and 300 µg/liter for the Group II compounds. The aliquots were stored at 4°C in the dark. At specific time intervals (0, 2, 4, 6, 8, 24, 48, and 72 h) aliquots were removed and fractionated. The fractions were analyzed by the extractables protocol (Method Appendix) with the exception that extract cleanup was omitted.

Results and Discussion--

The concentrations of Group I, II, and IV compounds measured in the supernatants and solids fractions of spiked Platte County primary sludge at 0 to 72 h following spiking are shown in Tables 66 to 68. Equilibration of the spikes between the solids and supernatant fractions appeared to have been achieved within the first 2 h following spiking. The recoveries of some compounds were decreased at longer equilibration times. Hence, the phase distribution experiments were conducted allowing only 2 h for equilibration. Significant losses of the spiked compounds were not observed for most compounds, with the exception of benzidine; the total recoveries were greater than 50%.

TABLE 65. RECOVERIES OF THE EXTRACTABLE COMPOUNDS SPIKED INTO PRIMARY POTW SLUDGE DILUTED TO 1% SOLIDS

Compound	Spike level (μg/L)	Platte County			
		Supernatant		Reconstituted solids	
		Unspiked level (μg/L)	Spike recovery (%)	Unspiked level (μg/L)	Spike recovery (%)
Group I					
1,4-Dichlorobenzene	1,000	ND	61, 80	ND	80, 45
Hexachloroethane	1,000	ND	210, 210	ND	80, 34
Bis(2-chloroethyl)ether	1,000	ND	46, 49	ND	190, 65
2,6-Dinitrotoluene	1,007	ND	110, 110	ND	220, 100
3,3'-Dichlorobenzidine	300	ND	150, 170	ND	47, 48
Benzidine	300	ND	74, 280	ND	0, 0
Group II					
Acenaphthylene	300	ND	200, 170	ND	64, 61
Fluoranthene	300	6	200, 190	ND	63, 64
n-Butylbenzylphthalate	300	22	55, 100	65	63, 51
Bis(2-ethylhexyl)phthalate	300	252	18, 63	556	55, 40
Group IV					
Phenol	1,180	ND	77, 84	ND	120, 110
2,4-Dimethylphenol	1,030	ND	77, 83	ND	74, 68
2,4-Dichlorophenol	1,160	ND	92, 95	ND	120, 120
Pentachlorophenol	1,160	ND	180, 96	ND.	121, 134

(continued)

TABLE 65 (concluded)

Compound	Spike level (μg/L)	Blue River Supernatant Unspiked level (μg/L)	Blue River Supernatant Spike recovery (%)	Blue River Reconstituted solids Unspiked level (μg/L)	Blue River Reconstituted solids Spike recovery (%)
Group I					
1,4-Dichlorobenzene	1,110	ND	52, 66	ND	70, 57
Hexachloroethane	1,110	ND	0, 0	ND	64, 70
Bis(2-chloroethyl)ether	1,010	ND	58, 88	ND	91, 94
2,6-Dinitrotoluene	1,010	ND	0, 0	ND	66, 64
3,3'-Dichlorobenzidine	1,040	ND	130, 120	ND	120, 93
Benzidine	985	ND	120, 180	ND	0, 0
Group II					
Acenaphthylene	307	20	61, 75	84	110, 100
Fluoranthene	320	80	77, 89	478	100, 110
n-Butylbenzylphthalate	342	478	78, 67	2,270	180, 120
Bis(2-ethylhexyl)phthalate	332	382	35, 40	815	130, 120
Group IV					
Phenol	1,080	63	110, 102	ND	130, 86
2,4-Dimethylphenol	1,030	9	120, 92	14	130, 86
2,4-Dichlorophenol	1,160	ND	140, 114	ND	160, 130
Pentachlorophenol	1,000	20	120, 90	73	200, 150

TABLE 66. RESULTS OF EQUILIBRATION STUDY OF GROUP I COMPOUNDS SPIKED INTO PLATTE COUNTY PRIMARY SLUDGE AT 5,000 μg/ℓ

Compound	Time (h)	Concentration				Average spike recovery (%)
		Supernatant (μg/L)		Solids (ng/g)		
1,4-Dichlorobenzene	0	390	400	1,380	1,580	40
	2	660	750	2,680	1,680	58
	4	860	910	2,790	2,580	71
	6	375	1,040	2,910	2,960	73
	8	960	940	2,560	2,630	71
	24	960	840	2,400	3,140	73
	48	900	1,160	2,410	2,080	66
	72	800	860	2,510	2,560	67
Hexachloroethane	0	160	250	2,025	2,150	46
	2	260	300	3,560	2,460	66
	4	600	510	2,560	3,000	67
	6	310	625	3,510	3,520	80
	8	340	370	1,890	2,360	50
	24	375	390	1,240	1,090	31
	48	260	300	1,890	1,750	42
	72	210	240	525	375	14
Bis(2-chloroethyl)ether	0	2,100	3,110	ND	400	56
	2	3,040	3,360	210	275	69
	4	4,920	5,160	ND	ND	100
	6	2,025	7,100	ND	ND	91
	8	5,010	4,880	200	340	100
	24	4,590	4,090	260	225	92
	48	4,820	6,720	250	210	120
	72	5,450	5,740	200	310	120
2,6-Dinitrotoluene	0	1,950	3,150	210	310	55
	2	2,550	2,860	350	390	60
	4	3,050	3,310	80	175	65
	6	2,020	3,120	500	150	57
	8	2,450	2,710	118	ND	52
	24	1,950	1,880	68	58	39
	48	1,280	1,440	210	150	30
	72	1,650	1,380	ND	ND	30
Benzidine[a]	0	ND	ND	ND	ND	0
	2	ND	ND	ND	ND	0
	4	78	82	ND	ND	27
	6	46	42	ND	ND	15
	8	56	59	ND	ND	19
	24	130	120	ND	ND	30
	48	b	ND	ND	ND	0
	72	ND	ND	ND	ND	0
3,3'-Dichlorobenzidine[a]	0	54	50	240	200	90
	2	44	41	260	300	110
	4	44	54	200	200	83
	6	46	42	ND	ND	7
	8	46	67	410	760	220
	24	300	225	700	750	330
	48	b	ND	175	175	58
	72	36	ND	200	190	71

a Spiking level 300 ppb.

b Extract lost during workup.

TABLE 67. RESULTS OF EQUILIBRATION STUDY OF GROUP II COMPOUNDS SPIKED INTO PLATTE COUNTY PRIMARY SLUDGE AT 300 μg/L

Compound	Time (h)	Concentration				Average spike recovery (%)
		Supernatant (μg/L)		Solids (ng/g)		
Acenaphthylene	0	430	36	225	212	84
	2	24	29	212	250	86
	4	26	25	150	137	56
	6	24	14	137	137	52
	8	16	14	150	162	57
	24	30	26	100	118	46
	48	a	20	137	116	48
	72	26	27	119	137	52
Fluoranthene	0	25	26	300	275	100
	2	20	21	287	375	110
	4	19	21	225	187	73
	6	18	12	212	187	71
	8	13	15	300	375	110
	24	35	34	312	325	120
	48	a	18	237	175	73
	72	30	23	225	212	80
n-Butylbenzylphthalate	0	16	14	287	250	73
	2	10	11	287	312	79
	4	18	19	225	225	62
	6	15	21	187	137	46
	8	ND	36	761	850	210
	24	95	32	800	850	230
	48	a	14	275	212	66
	72	24	16	150	250	56
Bis(2-ethylhexyl)phthalate	0	100	124	775	761	b
	2	89	87	900	875	
	4	42	49	525	437	
	6	60	107	625	562	
	8	61	225	3,060	3,700	
	24	425	362	2,400	2,825	
	48	a	64	575	437	
	72	77	76	512	512	

a Extract lost during workup.

b Recoveries were not determined since the unspiked level was higher than the spike level.

TABLE 68. EQUILIBRATION STUDY OF GROUP IV COMPOUNDS SPIKED INTO PLATTE COUNTY PRIMARY SLUDGE AT 5,000 μg/L

Compound	Time (h)	Concentration				Average spike recovery (%)
		Supernatant (μg/L)		Solids (ng/g)		
Phenol	0	6,160	5,890	790	725	140
	2	5,050	5,700	300	540	120
	4	4,760	5,710	550	660	120
	6	6,560	6,250	600	410	140
	8	7,600	6,725	425	425	150
	24	4,850	4,880	425	410	110
	48	4,740	4,910	440	410	110
	72	a	5,440	a	350	120
2,4-Dimethylphenol	0	5,260	4,710	740	775	120
	2	4,190	4,690	590	540	100
	4	4,090	4,540	425	400	95
	6	5,320	4,850	460	450	110
	8	7,520	6,010	510	525	150
	24	7,040	3,990	350	390	88
	48	3,730	3,810	490	525	86
	72	a	5,440	a	350	120
2,4-Dichlorophenol	0	3,350	2,950	2,050	2,180	110
	2	2,780	3,040	2,050	2,100	99
	4	2,560	2,950	1,890	2,150	96
	6	5,025	2,890	2,100	1,520	95
	8	4,200	3,580	1,950	2,060	120
	24	2,300	2,440	1,680	1,720	31
	48	2,110	2,340	1,520	1,790	79
	72	a	2,840	a	1,600	89
Pentachlorophenol	0	1,450	1,430	3,550	3,580	b
	2	875	750	4,120	4,250	
	4	690	900	4,310	4,110	
	6	700	940	4,250	4,060	
	8	950	1,240	4,050	3,760	
	24	825	940	4,180	4,060	
	48	825	1,150	4,130	3,350	
	72	a	775	a	4,220	

[a] Extract lost during workup.

[b] Recoveries were not determined. Analyses of pentachlorophenol in the solids fraction were hindered by severe interferences. The amount in the solids was determined by the difference between the spike level and the amount in the supernatant. Pentachlorophenol was not found in the unspiked sample and supernatant analyses had no interferences.

Determination of Phase Distributions

Experimental--

Sludge aliquots containing 0.80-g solids were diluted to 80 ml in 200-ml centrifuge tubes with glass-distilled water spiked with the extractable spiking compounds. The final spike concentrations were nominally 300, 1,000, 5,000, and 10,000 µg/liter for the Group I and IV compounds; 200, 300, and 3,000 µg/liter for the acenaphthylene and bis(2-ethylhexyl)phthalate; and 200 and 300 µg/liter for fluoranthene and butylbenzylphthalate. The spiked aliquots were stored at 4°C in the dark for 2 h before fractionating and analyzing as described in the preceding experiment. All experiments were conducted in duplicate.

Results and Discussion--

The concentrations of analytes determined in the supernatants and solids of the spiked sludge aliquots are shown in Tables 69 to 71 along with the phase distribution coefficients determined for each experiment. The phase distribution coefficients are summarized in Table 72. The phase distribution coefficients observed range from less than 10 for bis(2-chloroethyl)ether, 2,6-dinitrotoluene, benzidine, and phenol to greater than 4,000 for hexachloroethane, fluoranthene, and butylbenzylphthalate. The large relative standard deviations for the distribution coefficients shown in Table 72 for some compounds may be indicative of a relationship between spike concentration and the distributions. However, no well-defined concentration-distribution relationships were discernible.

TABLE 69. PHASE DISTRIBUTION COEFFICIENTS DETERMINED BY GROUP I COMPOUNDS SPIKED INTO PRIMARY POTW SLUDGE

Compound	Platte County POTW sludge				Blue River sludge			
	Spike level (µg/L)	Concentration			Spike level (µg/L)	Concentration		
		Supernatants (µg/L)	Solids (ng/g dry solids)	K distribution[a]		Supernatants (µg/L)	Solids (ng/g dry solids)	K distribution[a]
1,4-Dichlorobenzene	307	39 32	5,900 5,500	151 172	334	34 27	14,160 16,420	420 610
	1,027	325 237	32,500 38,800	100 164				
	5,000	950 1,075	431,000 270,000	454 251	5,575	900 780	231,800 41,400	260 53
	11,025	8,260 6,050	470,000 637,000	57 105	11,150	3,810 4,130	1,816,900 1,343,700	570 325
Hexachloroethane	320	ND[b] ND	12,500 11,900	c c	330	ND ND	12,740 12,650	c c
	1,067	47 29	50,000 50,000	1,064 1,720				
	5,000	125 150	625,000 431,000	5,000 2,870	5,500	ND ND	163,600 49,800	c c
	10,675	800 487	622,000 940,000	780 1,930	11,000	ND 110	1,509,300 888,100	c 8,070
Bis(2-chloroethyl)ether	300	225 212	ND ND	c c	305	170 133	ND ND	c c
	1,000	1,440 912	6,800 6,300	5 7				
	5,025	6,325 7,000	16,200 21,200	2.6 3	5,090	4,100 3,380	22,580 20,030	5.5 6
	10,000	42,190 31,000	11,200 28,700	0.3 0.9	10,170	19,400 19,600	77,660 32,120	3.8 1.6
2,6-Dinitrotoluene	360	175 187	2,200 2,200	13 12	304	ND ND	11,250 ND	c c
	1,200	812 687	8,400 10,600	10 15				
	5,040	2,310 2,600	21,200 23,700	9 9	5,080	ND ND	49,400 59,800	c c
	12,025	14,090 12,050	84,000 109,000	6 9	10,150	ND ND	130,600 94,800	c c

(continued)

TABLE 69 (concluded)

	Platte County POTW sludge				Blue River sludge			
		Concentration				Concentration		
Compound	Spike level (µg/L)	Supernatants (µg/L)	Solids (ng/g dry solids)	$K_{distribution}$[a]	Spike level (µg/L)	Supernatants (µg/L)	Solids (ng/g dry solids)	$K_{distribution}$[a]
Benzidine	295	ND	ND	c	295	235	ND	c
		ND	ND	c		660	ND	c
	990	1,660	16,000	10	4,920	1,142	29,250	26
		3,050	15,000	5		1,700	18,100	11
	9,850	30,500	253,750	8	9,850	6,170	74,250	12
		39,270	258,750	7		10,430	178,750	17
3,3'-Dichlorobenzidine	310	38	93,800	2,470	310	18	20,200	1,120
		48	93,800	1,950		20	19,900	1,000
	1,035	360	365,000	1,010	5,160	400	250,600	630
		275	325,000	1,180		330	331,000	1,000
	10,350	3,060	2,010,000	660	10,340	1,360	1,500,000	1,100
		2,620	2,000,000	760		1,490	1,513,000	1,040

a $K_{distribution} = \frac{\text{concentration of analyte in solids (ng/g)}}{\text{concentration of analyte in supernatant (µg/L)}}$.

b ND = not detected.

c $K_{distribution}$ could not be determined.

TABLE 70. PHASE DISTRIBUTION COEFFICIENTS DETERMINED FOR GROUP II COMPOUNDS SPIKED INTO PRIMARY POTW SLUDGE

Compound	Platte County POTW sludge				Blue River sludge			
	Spike level (µg/L)	Concentration		$K_{distribution}$[a]	Spike level (µg/L)	Concentration		$K_{distribution}$[a]
		Supernatants (µg/L)	Solids (ng/g dry solids)			Supernatants (µg/L)	Solids (ng/g dry solids)	
Acenaphthylene	202	17 18	23,810 14,890	1,400 830	308	38 46	21,870 22,800	580 500
	300	13 16	33,730 39,680	2,590 2,480				
	2,970	235 249	378,970 373,020	1,610 1,500	3,400	445 470	373,460 361,210	840 770
Fluoranthene	212	8 7	31,250 37,110	3,910 5,300				
	300	10 11	45,470 58,590	4,550 5,330	320	31 36	58,380 53,300	1,880 1,480
n-Butylbenzylphthalate	224	23 25	48,250 72,370	2,100 2,890				
	304	13 14	51,050 54,820	3,930 3,920	338	241 342	170,520 176,370	710 510
	3,270	125 125	539,470 605,260	4,320 4,840	3,270	589 697	466,700 446,900	790 500
Bis(2-ethylhexyl)phthalate	220	207 195	265,620 192,700	1,280 990				
	300	217 212	187,500 182,290	860 860	332	258 284	87,000 83,500	340 290

[a] $K_{distribution} = \frac{\text{concentration of analyte in solid (ng/g)}}{\text{concentration of analyte in supernatant (µg/L)}}$.

TABLE 71. PHASE DISTRIBUTION COEFFICIENTS DETERMINED FOR GROUP IV COMPOUNDS SPIKED INTO PRIMARY POTW SLUDGE

Compound	Platte County POTW sludge				Blue River sludge			
	Spike level (µg/L)	Concentration		$K_{distribution}$[a]	Spike level (µg/L)	Concentration		$K_{distribution}$[a]
		Supernatants (µg/L)	Solids (ng/g dry solids)			Supernatants (µg/L)	Solids (ng/g dry solids)	
Phenol	115	156	3,050	20	323	280	3,360	12
		162	b	b		433	5,270	12
	1,150	1,510	16,860	11	5,390	6,260	60,000	10
		1,590	17,860	11		6,320	47,270	8
	5,010	6,240	25,210	4	10,780	9,420	b	c
		7,040	45,170	6		10,100	103,640	10
	11,480	23,980	154,400	6				
		21,380	157,560	7				
2,4-Dimethylphenol	100	24	1,940	81	308	550	16,360	30
		31	b	c		808	23,640	29
	1,000	940	26,410	28	5,140	15,250	510,900	33
		906	24,650	27		13,300	498,200	37
	5,000	5,240	82,750	16	10,280	8,190	b	c
		5,860	75,700	13		8,480	258,200	30
	10,010	7,920	297,540	38				
		7,660	274,650	36				
2,4-Dichlorophenol	112	37	4,340	117	347	99	14,580	147
		37	b	c		142	22,200	156
	1,130	520	51,910	100	5,790	2,620	425,000	162
		540	48,730	90		2,780	435,400	157
	5,000	2,950	171,600	58	11,580	5,500	b	c
		3,230	178,000	55		5,610	713,200	127
	11,280	7,980	497,900	62				
		7,370	521,200	71				
Pentachlorophenol	114	ND	8,960	b	300	49	18,180	370
		ND	b	c		52	35,230	680
	1,130	152	71,850	473	5,000	1,260	471,000	370
		ND	89,570	b		1,250	476,700	390
	5,000	630	324,800	515	10,000	2,040	b	c
		540	334,650	620		2,020	693,200	340
	11,310	2,490	618,100	248				
		2,530	614,200	243				

[a] $K_{distribution} = \frac{\text{concentration of analyte in solids (ng/g)}}{\text{concentration of analyte in supernatant (µg/L)}}$.

[b] Sample lost.

[c] $K_{distribution}$ could not be determined.

TABLE 72. SUMMARY TABLE OF PHASE DISTRIBUTION COEFFICIENTS

Compound	$K_{\text{distribution}}$	
	Platte County POTW sludge	Blue River sludge
1,4-Dichlorobenzene	182 ± 124	437 ± 151
Hexachloroethane	2,230 ± 1,540	8,070[a]
Bis(2-chloroethyl)ether	3.1 ± 2.5	4.2 ± 2
2,6-Dinitrotoluene	10.4 ± 2.8	b
Benzidine	7.5 ± 2	17 ± 7
3,3'-Dichlorobenzidine	1,340 ± 720	980 ± 180
Acenaphthylene	1,740 ± 680	670 ± 159
Fluoranthene	4,770 ± 680	1,680 ± 282
n-Butylbenzylphthalate	3,670 ± 1,000	627 ± 145
Bis(2-ethylhexyl)phthalate	1,000 ± 200	315 ± 35
Phenol	9.3 ± 5.4	10.4 ± 1.7
2,4-Dimethylphenol	34 ± 23	31.8 ± 3.3
2,4-Dichlorophenol	79 ± 24	150 ± 14
Pentachlorophenol	420 ± 168	430 ± 140

a Data questionable.

b Distribution coefficient not determined.

APPENDIX

METHOD 624-S

PROTOCOL FOR THE ANALYSIS OF PURGEABLE ORGANIC PRIORITY POLLUTANTS IN INDUSTRIAL AND MUNICIPAL WASTEWATER TREATMENT SLUDGE

1. Scope and Application

1.1 This method is used for the determination of purgeable (volatile) organics The complete list of compounds is provided in Table 1.

1.2 The method is for qualitative and quantitative analysis of these compounds in municipal and industrial wastewater treatment sludges. The procedure requires the use of a gas chromatography/mass spectrometer (GC/MS) as the final detector.

1.3 The method detection limit for each compound is very dependent on the compound characteristics and the particular sludge analyzed. However, typical detection limits are 2 to 5 µg/liter for publicly owned treatment works (POTW) sludges with 1 to 5% total solids.

1.4 This method is restricted to use by or under the supervision of analysts experienced in the use of purge and trap systems and GC/MS and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.

2. Summary of Method

2.1 An inert gas is bubbled through a 10-ml sludge aliquot contained in a specially designed purging chamber at ambient temperature. The purgeables are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the purgeables onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the purgeables which are then detected with a mass spectrometer.[1,2]

3. Interferences

3.1 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled. Impurities in the purge gas and organic compounds outgassing from the plumbing upstream of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from the interferences under the conditions of the analysis by running method blanks. Method blanks are run by charging the purging device with reagent water and analyzing it in the normal manner. The use of non-TFE plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

3.2 Samples can be contaminated by diffusion of volatile organic materials (particularly dichloromethane) through the septum seal into the sample during shipment and storage. A field blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

3.3 Cross-contamination can occur whenever high-level and low-level samples are analyzed sequentially. To reduce cross-contamination, it is recommended that the purging device and sample syringe be rinsed twice between samples with reagent water to check for cross-contamination. For samples containing large amounts of water-soluble materials, suspended solids, high-boiling compounds or high organohalide levels, it may be necessary to wash the purging device with a soap solution, rinse with distilled water, and then dry in a 105°C oven between analyses. The trap and other parts of the system are also subject to contamination; therefore, frequent bakeout and purging of the entire system may be required.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified[3-5] for the information of the analyst.

4.2 The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzene, carbon tetrachloride, chloroform, 1,4-dichlorobenzene, and vinyl chloride. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

5. Apparatus and Materials

5.1 Sampling

5.1.1 Vial - 25-ml capacity or larger, equipped with a screw cap with hole in center (Pierce No. 13075 or equivalent). Detergent wash, rinse with tap and distilled water, and dry at 105°C before use.

5.1.2 Septum - TFE-faced (Pierce No. 12722 or equivalent). Detergent wash, rinse with tap and distilled water, and dry at 105°C for 1 hr before use.

5.2 Sample Preparation

5.2.1 Purge and Trap System. Assemble the system as depicted in Figures 1 and 2. A commercial version, such as the Tekmar Liquid Sample Concentrator Model LSC-1, or its equivalent, may be modified for use by replacing the standard purge tube with the purge tube shown in Figure 3. The trap is packed according to Figure 4. In order to function properly, the trap must be packed in the following order: Place the glass wool plug in the inlet end of the trap and follow with the OV-1, Tenax®, silica gel, charcoal, and finally, a second glass wool plug. Reversing the packing order, i.e., placing the charcoal in the trap first, will cause the silica gel and Tenax® layers to become contaminated with charcoal dust causing poor desorption efficiencies. Install the trap so that the effluent from the purging device enters the Tenax® end of the trap.

5.2.2 Glassware

5.2.2.1 Screw-cap vials, 40 ml with TFE-lined caps.

5.2.2.2 Graduated cylinder. 10 ml.

5.2.2.3 Volumetric flasks, 10 ml and 50 ml.

5.2.2.4 Round-bottom flask (optional), 250 ml for sample compositing.

5.2.3 Analytical balance, for standards preparation.

5.2.4 Roller mill and 1/8-in. stainless steel ball bearings.

5.2.5 Catalytic gas purifier.

5.2.6 Purging gas, He or N_2, water compressed, high-purity grade.

5.2.7 Syringes, 10 µl, 25 µl, 100 µl, 1 ml, and 10 ml gas tight.

5.2.8 Magnetic stirring motor with 2- to 2.5 cm TFE-coated spin bar.

5.3 For Quantitation and Identification

Gas chromatograph/mass spectrometer/data system, Finnigan 4000 or equivalent. The GC/MS interface should be a glass jet separator. The computer system should allow acquisition and storage of repetitive scan data throughout the GC/MS runs. Computer software should be available to allow searching of GC/MS data for display of extracted ion current profiles (EICP) and integration of the peaks. The GC/MS should be fitted with a stainless steel or glass column packed with 0.2% Carbowax 1500 on Carbopack C, or equivalent. Typical column dimensions are 1/8-in. OD stainless steel or 2-mm ID glass and 2.4 to 2.8 m in length.

6. Reagents

6.1 Trap Materials

6.1.1 Methylsilicone packing - 3% OV-1 on Chromosorb-W (60/80 mesh) or equivalent.

6.1.2 2,6-Diphenylene oxide polymer - Tenax-GC® (60/80 mesh), chromatographic grade or equivalent.

6.1.3 Silica gel - Davison Grade 15 (35/60 mesh) or equivalent.

6.1.4 Coconut charcoal - Barnaby Chaney No. CA-580-26 (26 mesh), Lot No. M-2649 or equivalent.

6.2 Reagent Water (purgeable organic-free). Generate organic-free water by passing tap water through a carbon filter bed containing about 1 lb of activated carbon and purging overnight with prepurified nitrogen. A Millipore Super-Q Water System or its equivalent may be used to generate organic-free deionized water. Organic-free water can also be prepared by boiling distilled water for 15 min. While still hot, transfer to a glass-stoppered bottle. Cool to room temperature. Continuously purge the water during storage. Test organic-free water daily by analyzing according to the method described in Section 10.

6.3 Methanol. "Distilled in Glass" or equivalent, stored in original containers and used as received.

6.4 Analytical Standards

6.4.1 Primary Standards. Prepare standard stock solutions (at approximately 2 μg/μl) by adding, from a 100-μl syringe, 1 to 2 drops of the 99+% pure reference standard to methanol (9.8 ml) contained in a tared 10-ml volumetric flask (weighed to nearest 0.1 mg). Add the component so that the two drops fall into the alcohol and do not come in contact with the neck of the flask. Prepare gaseous standards, e.g., vinyl chloride, in a similar manner using a 10.0 ml valved gas-tight syringe with a 2-in. needle. Fill the syringe (10.0 ml) with the gaseous compound. Weigh the 10-ml volumetric flask containing 9.8 ml of methyl alcohol to 0.1 mg. Lower the syringe needle to about 5 mm above the methyl alcohol meniscus and slowly inject the standard into the flask. The gas rapidly dissolves in the methyl alcohol. Reweigh the flask and use the weight gain to calculate the concentration of the standard. Dilute to volume, mix, and transfer to a 10-ml screw-cap vial with a silicone rubber/TFE cap liner. Gas stock standards are generally stable for at least 1 week when maintained at less than 0°C. With the exception of 2-chloroethylvinyl ether, stock standards of compounds that boil above room temperature are generally stable for at least 4 weeks when stored at 4°C. (Safety Caution: Because of the toxicity of most organohalides, dilutions should be made in a glove box suitable for handling carcinogens. It is advisable to use an approved respirator when high concentrations of such materials must be handled in a fume hood.)

6.4.2 Working Standards. From the primary dilutions, prepare 10 ml of a multicomponent secondary dilution mixture in methyl alcohol at a concentration of 50 ng/µl containing each of the compounds to be determined. Prepare 50 ml of a 50-ng/ml standard from the 50 ng/µl standard by dosing 50.0 µl into 50.0 ml of organic-free water. Additional working standards should be prepared as required to bracket concentrations of compounds for referee analyses.

6.5 Internal Standard Spiking Solution. From stock standard solutions prepared as above, add a volume to give 1,000 µg each of bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane to 45 ml of organic-free water (blank water) contained in a 50-ml volumetric flask, mix, and dilute to volume. Dose 9.0 µl of this internal standard spiking solution into every sample and reference standard analyzed. Prepare a fresh method recovery spiking solution on a weekly basis.

6.6 Surrogate Standard Spiking Solution. Select a minimum of three surrogate compounds from Table 2. Prepare and store stock standard and spiking solutions as described in Section 6.5

7. Calibration

7.1 Establish GC/MS operating parameters equivalent to those indicated in Section 11. The purge-trap GC/MS system can be calibrated using the external standard technique (Section 7.2) or the internal standard technique (Section 7.3).

7.2 External Standard Calibration Procedure

7.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to 10.0-ml aliquots of reagent water. Analyze immediately. One of the external standards should be at a concentration near, but above, the method detection limit, and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.2.2 Analyze each calibration standard with the purge-trap GC/MS system described in Section 11. Tabulate peak heights or area responses against the concentration of the analyte in the standard. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration analyzed (calibration factor) is a constant over the working range (< 10% relative standard deviation, RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.2.3 Verify the working calibration curve or calibration factor on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ± 10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor must be prepared for that compound.

7.3 Internal Standard Calibration Procedure. To use this approach, select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. The internal standards used for this procedure should include bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane.

7.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a 10.0-ml aliquot of reagent water, add 9.0 μl of the internal standard spiking solution, and analyze immediately. One of the standards should be at a concentration near, but above, the method detection limit and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.3.2 Analyze each calibration standard with the purge-trap GC/MS system described in Section 11. Tabulate peak height or area responses against concentration for each compound and internal standard. Calculate relative response factors (RRF) for each compound using Equation 1.

$$RRF = (A_s B_{is})/(A_{is} B_s) \qquad \text{(Eq. 1)}$$

where: A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

B_{is} = Mass of the internal standard (ng).

B_s = Mass of the parameter to be measured (ng).

If the RRF value over the working range is a constant (< 10% RSD), the RRF can be assumed to be nonvariant and the average RRF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is}, vs. RRF.

7.3.3 Verify the working calibration curve or RRF on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ± 10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

7.4 Daily Calibration of the Gas Chromatography-Mass Spectrometry (GC/MS) System

7.4.1 Evaluate the system performance each day that it is used for the analysis of samples or blanks by injecting 20 ng of p-bromofluorobenzene (BFB) into the GC inlet. Check to be sure that the performance criteria listed in Table 3 are met. If the criteria are not met, the instrument must be retuned to satisfy those criteria before continuing.

To perform the calibration test, the following instrumental parameters are required.

Electron energy, 70 eV (nominal)
Mass range, m/e 20-275
Scan time to provide at least 5 scans per peak, typically 5 s or less.

7.4.2 At the beginning of each working day, verify the calibration of the system by analyzing a standard (Section 7.3.3).

8. Quality Control

Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that is generated. Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.1. In recognition of the rapid advances that are occurring in chromatography, the analyst is permitted certain options to improve the separations or lower the cost of measurements. Each time such modifications are made to the method, the analyst is required to repeat the procedure in Section 8.1. The laboratory must spike all samples with surrogate standards to monitor continuing laboratory performance. This procedure is described in Section 8.4.

8.1 Demonstrate Acceptable Performance. Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this procedure.

8.1.1 For each compound to be measured, select a spike concentration representative of the expected levels in the samples. Using stock standards, prepare a quality control check standard in methanol 1,000 times more concentrated than the selected concentrations.

8.1.2 Syringe 10.0 µl of the check standard to each of a minimum of four 10.0-ml aliquots of reagent water. A representative sludge can be used in place of the reagent water, but one or more additional aliquots must be analyzed to determine background levels, and the spike level must exceed twice the background level for the test to be valid. Analyze the aliquots according to the method beginning in Section 10.

8.1.3 Calculate average recovery (R) and standard deviation (s), in percentage recovery, for the results. Sludge background corrections must be made before R and s calculations are performed.

8.1.4 Using the appropriate data from Table 7, determine the recovery and single operator precision expected for the method for each parameter, and compare these results to the values calculated in Section 8.1.3. If the data are not comparable, the analyst must review potential problem areas and repeat the test.

8.2 Precision and Accuracy Statement. The analyst must calculate method performance criteria for each of the surrogate standards.

8.2.1 Calculate upper and lower control limits for method performance for each surrogate standard, using the values for R and s calculated in Section 8.1.3:

Upper Control Limit (UCL) = R + 3 s
Lower Control Limit (LCL) = R - 3 s

The UCL and LCL can be used to construct control charts[6] that are useful in observing trends in performance.

8.2.2 For each surrogate standard, the laboratory must develop and maintain separate accuracy statements of laboratory performance for wastewater samples. An accuracy statement for the method is defined as R ± s. The accuracy statement should be developed by the analysis of four aliquots of sludge as described in Section 8.1.2, followed by the calculation of R and s. Alternately, the analyst may use four sludge data points gathered through the requirement for continuing quality control in Section 8.4. The accuracy statements should be updated regularly.[6]

8.3 Surrogate Spikes. The laboratory is required to spike all of their samples with the surrogate standard spiking solution to monitor spike recoveries. If the recovery for any surrogate standard does not fall within the control limits for method performance, the results reported for that sample must be qualified as described in Section 13.3. The laboratory should monitor the frequency of suspect data to ensure that it remains at or below 5%.

8.4 System Blanks. Analyze daily an organic-free water blank to demonstrate that all interferences from the analytical system are under control. The intensities of EICPs for the internal standards gives an overall check of the system sensitivity.

8.5 Fortified and Replicate Samples

8.5.1 Sample Selection. Select at least 30% of all samples or at least one sample from each sampling location for fortified and replicate aliquot analysis. Analyze the selected samples in duplicate to determine unspiked analyte concentrations. Using the procedures described in Section 8.5.2, spike and analyze duplicate aliquots of the selected samples. Analyze a third unspiked aliquot of the selected samples on the same day that the corresponding spiked aliquots are analyzed.

8.5.2 Spiking Procedures. Determine the volume of an empty vial to within 0.5 ml by filling the vial with volatile organics-free water and then measuring the volume of water with a graduated cylinder. Mark the volume on the vial and allow it to air-dry. Add 3 to 5 precleaned ball bearings to the vial. Transfer the sample to the vial and spike with the representative purgeable compounds listed in Table 4 and other compounds identified in the sample, as available, at two times the concentration found in the unspiked sample or at 10 times the lower limit of detection, whichever is greater. Seal the vial and place on a roller mill in a 4°C cold room; tumble the sample for 16 h before analysis.

8.6 Field Blanks. Analyze a field blank for each day of sampling at each sampling location.

8.7 Additional Quality Control. It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should perform analysis of reference materials and participate in relevant performance evaluation studies.

9. Sampling and Preservation

9.1 Sampling. Samples must be collected in 40-ml screw-cap vials with zero headspace and sealed with TFE-lined septa. Before using, wash all sample bottles and TFE seals in detergent and rinse with tap water and finally distilled water. Allow the bottles and seals to air-dry at room temperature, heat in a 105°C oven for 1 h, then allow to cool in an area known to be free of organics.

NOTE: Do not heat the TFE seals for extended periods of time (more than 1 h) because the silicone layer slowly degrades at 105°C.

9.2 Preservation. Ice samples immediately after collection, refrigerate at 4°C, and purge within 10 days. Desorb and complete the analyses immediately after purging.

9.3 Special Preservation for Aromatics. Experimental evidence indicates that some aromatic compounds, notably benzene, toluene, and ethyl benzene are susceptible to rapid biological degradation under certain environmental conditions.[2] Refrigeration alone may not be adequate to preserve these compounds in sludges for more than 7 days. For this reason, a separate sample should be collected, acidified, and analyzed when these aromatics are to be determined. Collect about 500 ml of sample in a clean container. Adjust the pH of the sample to about 2 by adding HCl (1+1) while stirring. Check pH with narrow range (1.4 to 2.8) pH paper. Fill a sample container as described in Section 9.1. If chlorine residual is present, add sodium thiosulfate to another sample container and fill as in Section 9.1 and mix thoroughly.

10. Sample Preparation and Purging

10.1 Sample Compositing. Sludge samples for the analysis of purgeable compounds are typically collected as grab samples. Several samples may be composited with minimal analyte losses. Chill the appropriate sample vials and a clean 250-ml round-bottom flask by immersing them in an ice bath. Gently pour the entire contents of each vial into the flask and swirl gently. Vigorous mixing must be avoided to prevent analyte losses. Prepare a number of composite aliquots sufficient for subsequent analysis by gently pouring the composited sludge into precleaned 40-ml vials. Seal the vials with zero headspace using TFE-lined septa and screw-caps. Store the composited samples at 4°C.

10.2 Sample Purging. Condition the adsorbent trap at 200°C with nitrogen or helium flow. Allow the trap to cool to ambient room temperature and turn off the gas flow through the trap and purge tube before sample purging. Remove an aliqout of the sludge sample by gently pouring the sludge into a 10-ml graduated cylinder. Fill the cylinder just to the 10.0-ml mark. Dose the aliquot with 9 µl of the internal standard spiking solution by slowly injecting the solution (with a 10-µl syringe) 3 to 4 cm under the surface of the sludge. Gently pour the spiked sludge aliquot into the purge tube. If solids adhere to the inner walls of the graduated cylinder, rinse the cylinder with a small amount of organics-free water and add the rinsings to the purge tube. Seal the purge tube and turn on the purge gas flow (40 ml/min). Purge the sample for 12 min while maintaining the sample and trap at ambient room temperature.

11. Analysis of the Sample Purge

Analyze the sample purge by GC/MS using the Carbowax 1500/Carbopack C column described in Section 5.2 operated with a helium carrier gas flow of 30 ml/min. Heat the trap to 180 to 200°C. Backflush it for 3 min into the gas chromatograph, with the oven at 40°C. At the end of the 3-min period, program the column at 10°C/min to 170°C. Hold at this temperature until all compounds have eluted. An example of the separation achieved by this column is shown in Figure 5. Relative retention times for the purgeable compounds are listed in Table 5. The purging device must be removed from the instrument and thoroughly rinsed with volatile organic-free water between each sample. The trap must be conditioned at 200°C with flow for 10 min between each sample.

12. Qualitative Identification

12.1 Obtain EICPs for the primary ion (Table 5) and, if available, at least two secondary ions for each parameter of interest. The following criteria must be met to make a qualitative identification.

12.1.1 The characteristic ion of each parameter of interest must maximize in the same or within one scan of each other.

12.1.2 The retention time must fall within ± 30 s of the retention time of the authentic compound.

12.1.3 The relative peak heights of the three characteristic ions in the EICPs must fall within ± 20% of the relative intensities of these ions in a reference mass spectrum. The reference mass spectrum can be obtained from a standard analyzed in the GC/MS system or from a reference library.

12.2 Structural isomers that have very similar mass spectra and less than 30 s difference in retention time, can be explicitly identified only if the resolution between authentic isomers in a standard mix is acceptable. Acceptable resolution is achieved if the baseline to valley height between the isomers is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

13. Calculations

13.1 When a parameter has been identified, the quantitation of that parameter should be based on the integrated abundance from the EICP of the first listed characteristic ion given in Table 5. If the sample produces an interference for the primary ion, use a secondary characteristic ion to quantitate. Quantitation may be performed using the external or internal standard techniques.

13.1.1 If the external standard calibration procedure is used, calculate the concentration of the parameter being measured from the area of the characteristic ion using the calibration curve or calibration factor in Section 7.2.

13.1.2 If the internal standard calibration procedure was used, calculate the concentration in the sample using the relative response factor (RRF) determined in Section 7.3 and Equation 2.

$$\text{Concentration } \mu g/L = \frac{(A_s)(B_{is})}{(A_{is})(RRF)(V)} \qquad \text{(Eq. 2)}$$

where: A_s = Area of the characteristic ion for the parameter or surrogate standard to be measured.

A_{is} = Area of the characteristic ion for the internal standard.

B_{is} = Mass of the internal standard (ng).

V = Volume of sample purged (ml).

13.2 Report results in micrograms per liter. The results for cis- and trans-1,3-dichloropropene should be reported as total 1,3-dichloropropene (Storet No. 34561, CAS No. 542-75-6). When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

13.3 If any of the surrogate standard recoveries fall outside the control limits which were established as directed in Section 8.3, data for all parameters in that sample must be labeled as suspect.

14. Method Performance

Performance data for the application of this method to both POTW and industrial sludges are shown in Table 7. These data were generated by analyzing duplicate aliquots of unspiked sludge and triplicate aliquots of sludge spiked at 2, 20, and 200 times the typical detection limits for representative purgeable compounds. The method was evaluated using three POTW sludges and two industrial sludges. The recoveries and standard deviations represent the results from all determinations from each sludge type. The mean RSD for triplicates illustrate the precision for triplicate analyses. Although the recoveries observed were generally good, many recovery determinations were influenced by relatively high concentrations of the spiking compounds in the unspiked sludges. In most cases, the results of recovery determinations for compounds present in the unspiked samples at concentrations in excess of the spiking level were not included in Table 7. The small mean RSD for triplicates observed for most compounds indicate that the largest component of the method variance can be attributed to differences in the characteristics of the test sludges. These data represent the results from one laboratory.

15. References

1. Bellar, T. A., and J. J. Lichtenberg, Journal American Water Works Association, 66, p. 739 (1964).
2. Bellar, T. A., and J. J. Lichtenberg, "Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds," Measurement of Organic Pollutants in Water and Wastewater, C. E. Van Hall, editor, American Society for Testing and Materials, Philadelphia, PA. Special Technical Publication 686, 1978.
3. "Carcinogens - Working with Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute of Occupational Safety and Health, Publication No. 77-206, August 1977.
4. "OSHA Safety and Health Standards, General Industry," (29CFR1910), Occupational Safety and Health Administration, OSHA 2206 (Revised January 1976).
5. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.
6. "Handbook of Analytical Quality Control in Water and Wastewater Laboratories," EPA-600/4-79-019, U.S. Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1979.

16. Additional Sources

1. "Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants." U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, March 1977, Revised April 1977. Effluent Guidelines Division, Washington, DC 20460.

2. "Methods 330.4 (Titrimetric, DPD-FAS) and 330.5 (Spectrophotometric, DPD) for Chlorine, Total Residual," Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory - Cincinnati, OH 45268. In preparation.

3. "Preservation and Maximum Holding Time for the Priority Pollutants," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268. In preparation.

4. Budde, W. L., and J. W. Eichelberger, "Performance Tests for the Evaluation of Computerized Gas Chromatography/Mass Spectrometry Equipment and Laboratories," EPA-600/4-80-025, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, p. 16, April 1980.

5. Kleopfer, R. D., "Priority Pollutant Methodology Quality Assurance Review," U.S. Environmental Protection Agency, Region VII, Kansas City, KS. Seminar for Analytical Methods for Priority Pollutants, Norfolk, VA, January 17-18, 1980, U.S. Environmental Protection Agency, Office of Water Programs, Effluent Guidelines Division, Washington, D.C. 20460.

TABLE 1. PURGEABLE ORGANIC PRIORITY POLLUTANTS

Compound	CAS No.
Acrolein	107-02-8
Acrylonitrile	107-13-1
Chloromethane	74-87-3
Dichlorodifluoromethane	75-71-8
Bromomethane	74-83-9
Vinyl chloride	75-01-4
Chloroethane	75-00-3
Dichloromethane	75-09-2
Trichlorofluoromethane	75-69-4
1,1-Dichloroethene	75-35-4
1,1-Dichloroethane	75-34-3
trans-1,2-Dichloroethene	540-59-0
Chloroform	67-66-3
1,2-Dichloroethane	107-06-2
1,1,1-Trichloroethane	71-55-6
Carbon tetrachloride	56-23-5
Bromodichloromethane	75-27-4
1,2-Dichloropropane	78-87-5
Benzene	71-43-2
trans-1,3-Dichloropropene	542-75-6
Trichloroethene	79-01-6
cis-1,3-Dichloropropene	542-75-6
Dibromochloromethane	124-48-1
1,1,2-Trichloroethane	79-00-5
2-Chloroethylvinyl ether	110-75-8
Bromoform	75-25-2
Tetrachloroethene	127-18-4
Toluene	108-88-3
1,1,2,2-Tetrachloroethane	79-34-5
Chlorobenzene	108-90-7
Ethylbenzene	100-41-4

TABLE 2

SUGGESTED SURROGATE AND INTERNAL STANDARDS

Compound	Retention Time (minutes)[a]	Primary Ion	Secondary Ions
Surrogate Standards			
Benzene d-6	17.0	84	-
4-Bromofluorobenzene	28.3	95	174, 176
1,2-Dichloroethane d-4	12.1	102	-
1,4-Difluorobenzene	19.6	114	63,88
Ethylbenzene d-5	26.4	111	-
Ethylbenzene d-10	26.4	98	-
Fluorobenzene	18.4	96	70
Pentafluorobenzene	23.5	168	-
Internal Standards			
Bromochloromethane	9.3	128	49, 130, 51
2-Bromo-1-chloropropane	18.5	77	79, 156
1,4-Dichlorobutane	22.9	55	90, 92

[a] For chromatographic conditions, see Table 5.

TABLE 3. p-BROMOFLUOROBENZENE IONS AND ION ABUNDANCE CRITERIA[a]

m/e	Ion abundance criteria
50	25-40% of m/e 95
75	30-60% of m/e 95
95	base peak, 100% relative abundance
96	5-9% of m/e 95
173	< 2% of m/e 95
174	> 50% of m/e 95
175	5-9% of m/e 174
176	> 95% but < 101% of m/e 95
177	5-9% of m/e 176

[a] Eichelberger, J. W., L. E. Harris, and W. L. Budde, "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry Systems," Analytical Chemistry, 47, 995-1000 (1979).

TABLE 4. REPRESENTATIVE PURGEABLE COMPOUNDS FOR RECOVERY STUDIES

Benzene
Carbon tetrachloride
Chlorobenzene
Chloroform
1,2-Dichloroethane
1,1-Dichloroethene
Ethyl benzene
Tetrachloroethene
1,1,1-Trichloroethane
Trichloroethene
Vinyl chloride

TABLE 5. RELATIVE RETENTION TIMES OF PURGEABLE PRIORITY POLLUTANTS[a]

Compound	RRT[b]
Chloromethane	0.116
Bromomethane	0.146
Dichlorodifluoromethane	0.169
Vinyl chloride	0.179
Chloroethane	0.209
Dichloromethane	0.312
Trichlorofluoromethane	0.435
1,1-Dichloroethene	0.475
Bromochloromethane (IS)	0.502
1,1-Dichloroethane	0.545
trans-1,2-Dichloroethene	0.585
Chloroform	0.621
1,2-Dichloroethane	0.661
1,1,1-Trichloroethane	0.728
Carbon tetrachloride	0.751
Bromodichloromethane	0.784
Bis-chloromethyl ether	Unknown[c]
1,2-Dichloropropane	0.854
trans-1,3-Dichloropropene	0.870
Trichloroethene	0.900
Benzene	0.917
Dibromochloromethane	0.934
cis-1,3-Dichloropropene	0.937
1,1,2-Trichloroethane	0.937
2-Chloroethylvinyl ether	Unknown[d]
2-Bromo-1-chloropropane (IS)	1.000
Bromoform	1.073
1,1,2,2-Tetrachloroethane	1.206
Tetrachloroethene	1.213
1,4-Dichlorobutane (IS)	1.236
Toluene	1.292
Chlorobenzene	1.412
Ethylbenzene	1.641
Acrolein	Unknown[e]
Acrylonitrile	Unknown[e]

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[a] These data were obtained under the following conditions: GC column - glass, 8-ft long x 0.1 in. I.D. packed with Carbopack C (60/80 mesh), coated with 0.2% Carbowax 1500; carrier flow - 30 ml/min; oven temperature - initial 40°C held for 3 min, programmed 10°C/min to 170°C and held until all compounds eluted.

[b] Retention times relative to 2-bromo-1-chloropropane with an absolute retention time of 903 s.

[c] *Bis*-Chloromethyl ether has a half-life of about 10 s in aqueous mixtures.

[d] 2-Chloroethylvinyl ether may be unstable in aqueous mixtures. Retention time is unknown.

[e] Acrolein and acrylonitrile do not purge efficiently from aqueous mixtures. Retention times under these conditions are not known.

TABLE 6. CHARACTERISTIC IONS OF PURGEABLE ORGANICS

Compound	EI ions (relative intensity)	Ion used to quantify
Chloromethane	50(100); 52(33)	50
Bromomethane	94(100); 96(94)	94
Dichlorodifluoromethane	85(100); 87(33); 101(13); 103(9)	101
Vinyl chloride	62(100); 64(33)	62
Chloroethane	64(100); 66(33)	64
Dichloromethane	49(100); 51(33); 84(86); 86(55)	84
Trichlorofluoromethane	101(100); 103(66)	101
1,1-Dichloroethene	61(100); 96(80); 98(53)	96
Bromochloromethane (IS)	49(100); 130(88); 128(70); 51(33)	128
1,1-Dichloroethane	63(100); 65(33); 83(13); 85(8); 98(7); 100(4)	63
trans-1,2-Dichloroethene	64(100); 96(90); 98(57)	96
Chloroform	83(100); 85(66)	83
1,2-Dichloroethane	62(100); 64(33); 98(23); 100(15)	98
1,1,1-Trichloroethane	98(100); 99(66); 117(17); 119(16)	97
Carbon tetrachloride	117(100); 119(96); 121(30)	117
Bromodichloromethane	83(100); 85(66); 127(13); 129(17)	127
Bis-chloromethyl ether	79(100); 81(33)	79
1,2-Dichloropropane	63(100); 65(33); 112(4); 114(3)	112
trans-1,3-Dichloropropene	75(100); 77(33)	75
Trichloroethene	95(100); 97(66); 130(90); 132(85)	130
Benzene	78(100); 52(15)	78
Dibromochloromethane	129(100); 127(78); 208(13); 206(10)	127
cis-1,3-Dichloropropene	75(100); 77(33)	75
1,1,2-Trichloroethane	83(95); 85(60); 97(100); 99(63); 132(9); 134(8)	97
2-Chloroethylvinyl ether	63(95); 65(32); 106(18)	106
2-Bromo-1-chloropropane (IS)	77(100); 79(33); 156(5)	77
Bromoform	171(50); 173(100); 175(50); 250(4); 252(11); 254(11); 256(4)	173
1,1,2,2-Tetrachloroethane	83(100); 85(66); 131(7); 133(7); 166(5); 168(6)	168
Tetrachloroethene	129(64); 131(62); 164(78); 166(100)	164
1,4-Dichlorobutane (IS)	55(100); 90(30); 92(10)	55
Toluene	91(100); 92(78)	92
Chlorobenzene	112(100); 114(33)	112
Ethylbenzene	91(100); 106(33)	106
Acrolein	26(49); 27(100); 55(64); 56(83)	56
Acrylonitrile	26(100); 51(32); 52(75); 53(99)	53

TABLE 7. ACCURACY AND PRECISION FOR PURGEABLE ORGANICS

	Three POTW Sludges						Two Industrial Sludges					
				Spike Recovery						Spike Recovery		
		Spike level (µg/ℓ)						Spike Level (µg/ℓ)				
Compound	Determin-ations	Min	Max	Mean (%)	Standard devia-tion	Mean RSD for tripl. (%)	Determin-ations	Min	Max	Mean (%)	Standard devia-tion	Mean RSD for tripl. (%)
Benzene	17	1	100	160	55	16	15	1	100	98	25	16
Chloroform	23	2	200	100	58	20	17	2	200	76	22	20
1,1-Dichloroethane	27	5	500	170	53	15	15	5	500	110	51	28
Tetrachloroethane	15	3	300	150	33	16	12	3	300	150	70	24
Vinyl chloride	18	50	500	130	38	14	16	5	500	110	47	13
1,2-Dichloroethane	27	5	500	140	51	14	12	5	500	100	28	16
Trichloroethene	18	20	200	160	69	24	12	2	200	140	44	21
1,1,1-Trichloroethane	21	16	1,600	130	47	23	15	16	1,600	110	40	11
Chlorobenzene	21	2	200	120	36	16	15	2	200	160	62	14
Ethyl benzene	18	5	500	120	26	15	12	5	500	150	55	14

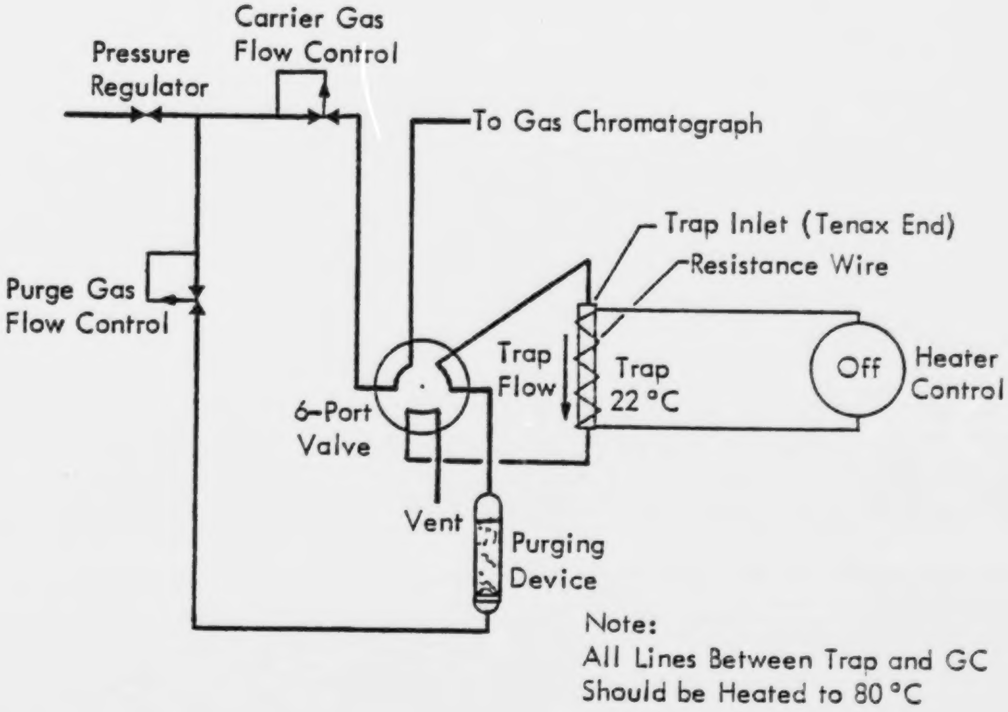
Carrier Gas
Flow Control
Pressure
Regulator
To Gas Chromatograph
Trap Inlet (Tenax End)
Resistance Wire
Purge Gas
Flow Control
Trap
Flow
Trap
22 °C
Off
Heater
Control
6-Port
Valve
Vent
Purging
Device
Note:
All Lines Between Trap and GC
Should be Heated to 80 °C

Figure 1. Schematic of the purge-trap system in the purge mode.

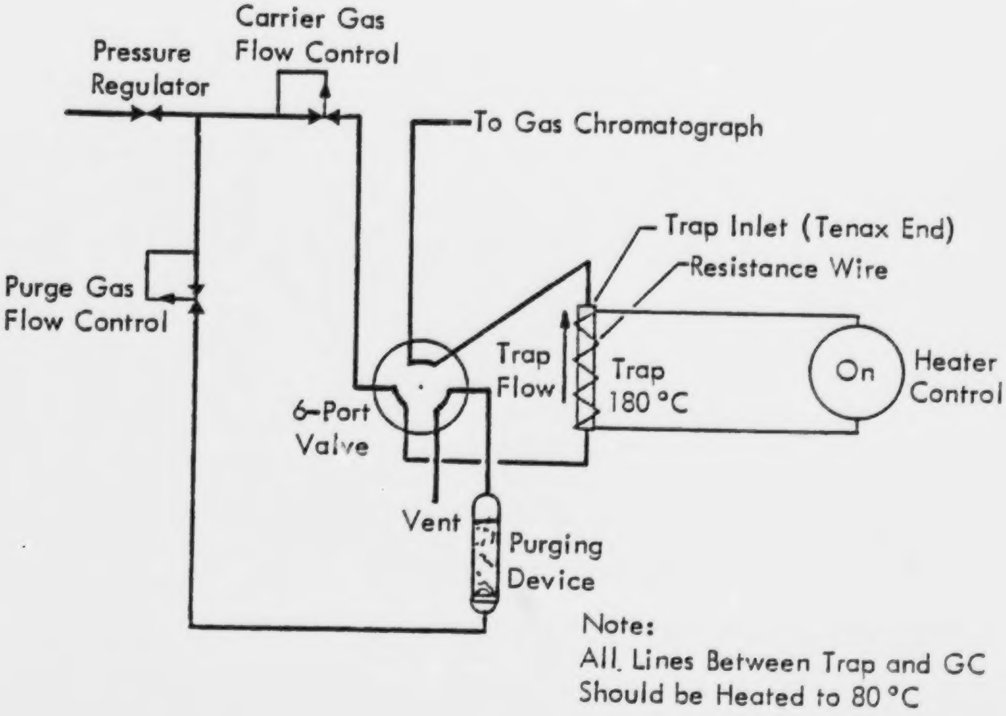
Carrier Gas
Flow Control
Pressure
Regulator
To Gas Chromatograph
Trap Inlet (Tenax End)
Resistance Wire
Purge Gas
Flow Control
Trap
Flow
Trap
180 °C
On
Heater
Control
6-Port
Valve
Vent
Purging
Device
Note:
All Lines Between Trap and GC
Should be Heated to 80 °C

Figure 2. Schematic of the purge-trap system in the desorb mode.

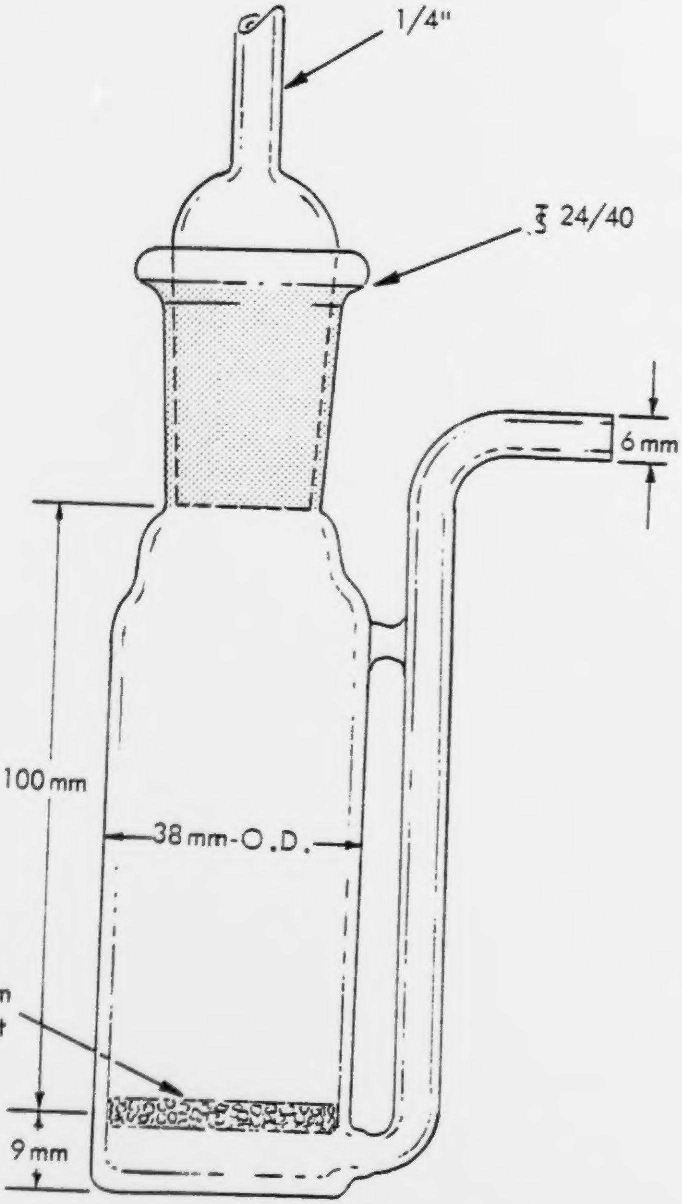
1/4"
$24/40
6 mm
100 mm
38 mm-O.D.
Medium Frit
9 mm

Figure 3. Bottom frit purge tube.

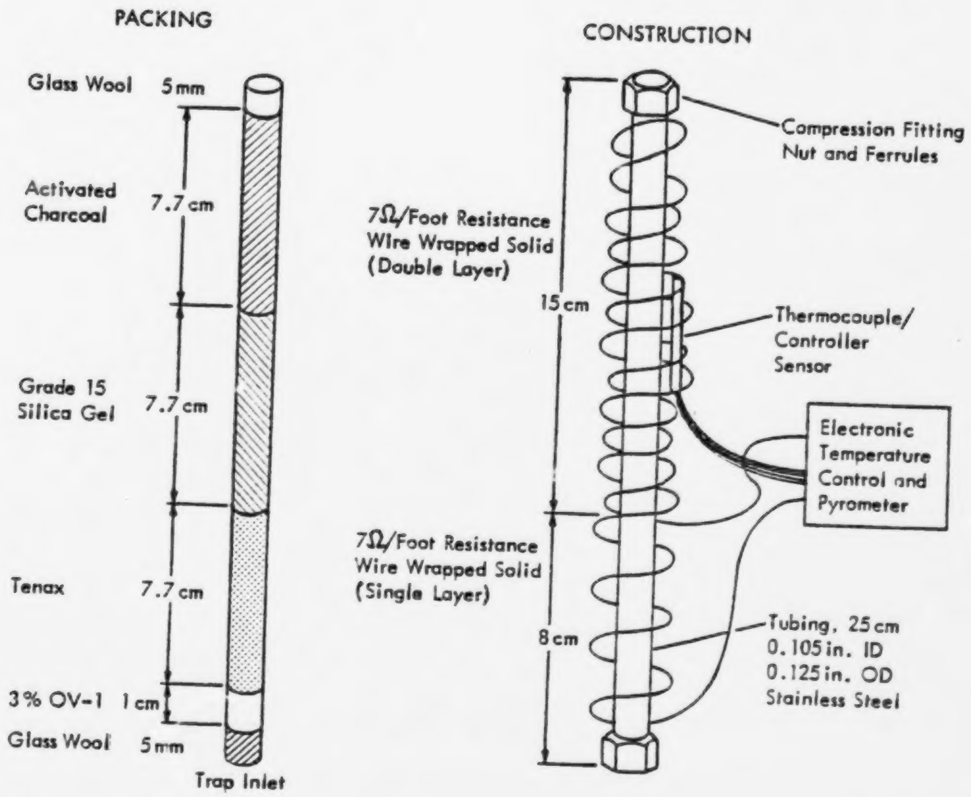
PACKING
Glass Wool 5 mm
Activated Charcoal 7.7 cm
Grade 15 Silica Gel 7.7 cm
Tenax 7.7 cm
3% OV-1 1 cm
Glass Wool 5 mm
Trap Inlet
CONSTRUCTION
Compression Fitting Nut and Ferrules
7Ω/Foot Resistance Wire Wrapped Solid (Double Layer)
15 cm
Thermocouple/ Controller Sensor
Electronic Temperature Control and Pyrometer
7Ω/Foot Resistance Wire Wrapped Solid (Single Layer)
8 cm
Tubing, 25 cm 0.105 in. ID 0.125 in. OD Stainless Steel

Figure 4. Trap packings and construction.

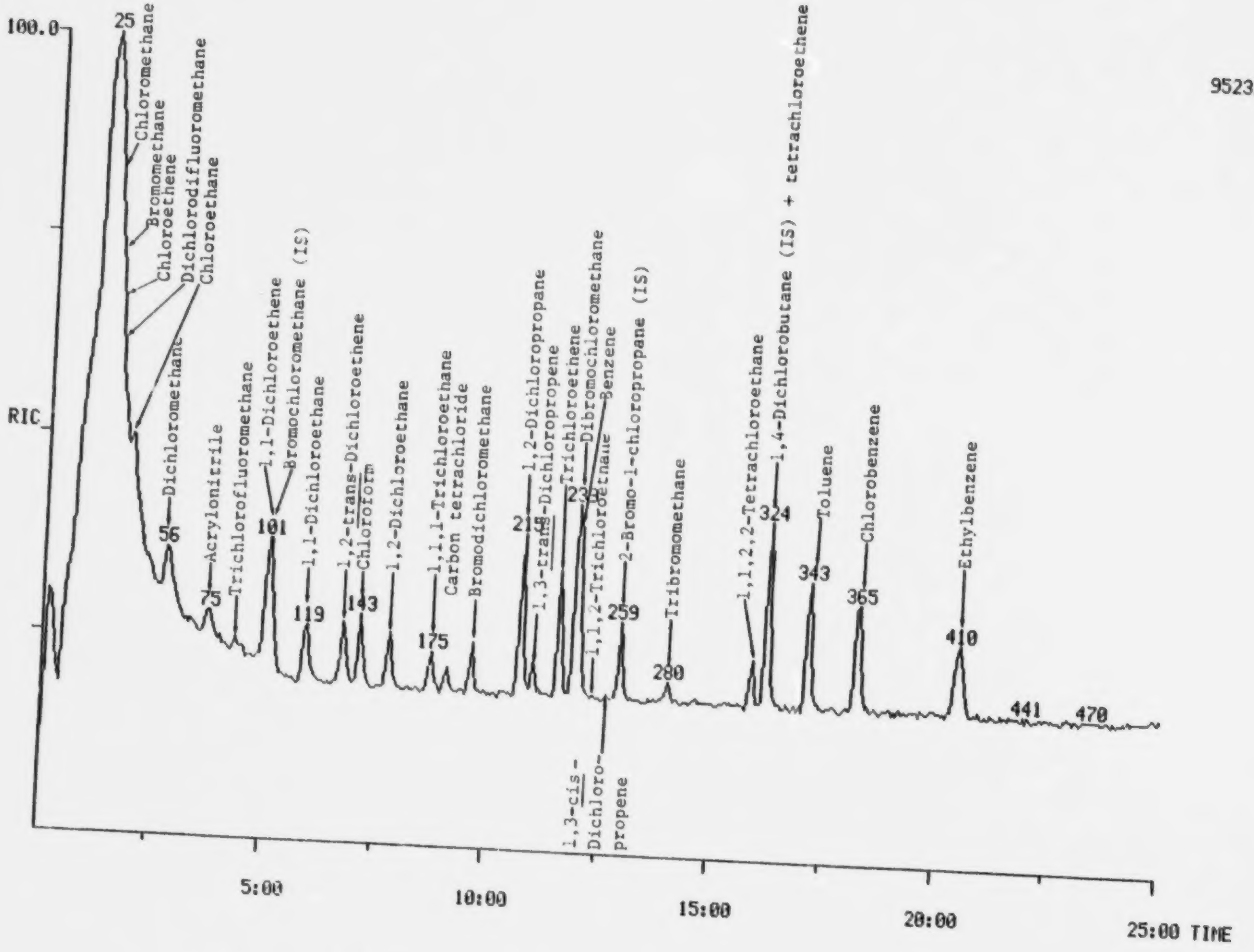

Figure 5. GC/MS chromatogram for the purgeable compounds.

METHOD 625-S

PROTOCOL FOR THE ANALYSIS OF EXTRACTABLE ORGANIC PRIORITY POLLUTANTS IN INDUSTRIAL AND MUNICIPAL WASTEWATER TREATMENT SLUDGE

1. Scope and Application

1.1 This method is used for the determination of the base, neutral, and acid-extractable organic compounds listed in Table 1.

1.2 The method is for qualitative and quantitative analysis of these compounds in municipal and industrial wastewater treatment sludges. The procedure requires the use of a gas chromatograph/mass spectrometer (GC/MS) as the final detector.

1.3 The method detection limit for each compound is dependent on the compound characteristics and the particular sludge analyzed. However, typical detection limits are 200 to 300 μg/liter for publicly owned treatment works (POTW) sludges with 1 to 5% total solids.

1.4 This method is restricted to use by or under the close supervision of experienced analysts. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.

2. Summary of Method

This method (Figure 1) uses repetitive solvent extraction aided by a high-speed homogenizer. The extract is separated by centrifugation and removed with a pipette or syringe. Sludges are extracted at pH $\geqq 11$ to isolate base/neutral compounds and at pH $\leqq 2$ to isolate acidic compounds. Extracts containing base/neutral compounds are cleaned by silica gel or florisil chromatography or by gel permeation chromatography (GPC). Extracts containing the acidic compounds are cleaned by GPC. The organic priority pollutants are determined in the cleaned extracts by capillary column or packed column GC/MS. Option A, i.e., extract cleanup by silica gel or florisil chromatography and analysis by capillary GC/MS (HRGC/MS) is preferred since HRGC/MS allows easier data interpretation. Qualitative identification of compounds is performed using the retention time and the relative abundance of three characteristic ions. Quantitative analysis is performed using external or internal standard techniques with a single characteristic ion.

3. Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in GC/MS chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.4.

3.1.1 Glassware must be scrupulously cleaned. All glassware should be cleaned as soon as possible after use by rinsing with the last solvent used in it. This should be followed by detergent washing with hot water, and rinses with tap water and reagent water. It should then be drained dry, and heated in a muffle furnace at 400°C for 15 to 30 min. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality dichloromethane may be substituted for the muffle furnace heating. Volumetric glassware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. It should be stored inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the wastewater treatment system being sampled. The cleanup procedures in Section 11 can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches to achieve acceptable detection limits.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis.

4.2 The following parameters covered by this method have been tentatively classified as known or suspected, human or mamalian carcinogens; benzo[a]anthracene, benzidine, 3,3'-dichlorobenzidine, benzo[a]pyrene, α-BHC, β-BHC, δ-BHC, γ-BHC, dibenzo[a,h]anthracene, N-nitrosodimethylamine, 4,4'-DDT, and polychlorinated biphenyls.

5. Apparatus and Materials

5.1 Sampling, Extraction, and Extract Cleanup

5.1.1 Emulsifier-Tekmar Tissumizer® or equivalent, high capacity.

5.1.2 Centrifuge, capable of handling 200 ml bottles.

5.1.3 Centrifuge bottles with TFE lined screw caps, 200 ml.

5.1.4 Kuderna-Danish (K-D) glassware.

5.1.4.1 Snyder columns, 3 bulb, macro.

5.1.4.2 Snyder columns modified micro.

5.1.4.3 Evaporating flasks, 500 ml, 250 ml.

5.1.4.4 Receiver ampuls 5 and 10 ml, graduated, with spring attachment.

5.1.4.5 Beakers, 100 ml.

5.1.5 Water or steam bath for Kuderna-Danish concentrations.

5.1.6 Chromatographic (drying) Column - Pyrex (400 mm x 20 mm ID) without a fritted plate.

5.1.7 Separatory funnels, 500 ml with TFE stopcock.

5.1.8 Syringe, 100 ml, Pyrex, with long needle.

5.1.9 Graduated cylinder, 100 or 250 ml.

5.1.10 Vials, 2 ml, 4 ml, and 8 ml with TFE lined screw caps.

5.1.11 Sample bottles, 1,000 ml or 4,000 ml glass with TFE lined screw caps.

5.1.12 Disposable pipettes, for transferring extracts.

5.1.13 Gel Permeation Chromatograph (GPC), Analytical Biochemical Labs, Inc., GPC Autoprep 1002 or equivalent including:

5.1.13.1 Glass column 25 mm ID x 60-70 mm packed with 70 g of Bio-Beads SX-3.

5.1.13.2 Chromatographic pump, operated at 5 ml/min with 350-700 millibars (5-10 psi).

5.1.13.3 Injector with loop.

5.1.13.4 Syringe filter holder, stainless steel and TFE, Gelman 4310 or equivalent.

5.1.13.5 Spectrophotometric chromatographic detector, 254 nm, with strip chart recorder (optional, for GPC calibration).

5.1.14 Chromatographic column, 200 mm x 20 mm ID, with solvent reservoir (250 ml) and TFE stopcock.

5.1.15 Roller mill.

5.1.16 Bottles, 500 ml, brown glass.

5.2 For Identification and Quantitation

5.2.1 Gas chromatograph/mass spectrometer with data system, Finnigan 4000 or equivalent. The GC/MS interface should include a glass jet separator and a direct capillary line. The computer system should allow acquisition and storage of repetitive scan data throughout the GC/MS runs. Computer software should be available to allow searching of GC/MS data for display of extracted ion current profiles (EICPs) and integration of the peaks. The GC injection port must be designed for on-column injection when using packed columns and for splitless or on-column injection when using capillary columns. GC columns required are:

5.2.1.1 0.9 to 1.8 m x 2 mm ID glass packed with 1% SP-1240-DA on 100/120 mesh Supelcoport or equivalent.

5.2.1.2 15-30 m x 0.2 mm ID wall coated open tubular capillary column coated with SE-54, or equivalent, providing at least 25,000 effective theoretical plates, measured at C_{13}, or a 1.8 m x 2 mm ID glass packed with 3% SP-2250 on 100/120 mesh Supelcoport, or equivalent.

5.2.2 Gas chromatograph/flame ionization detector with the same GC columns as for the GC/MS system.

6. Reagents

6.1 For Extraction and Extract Cleanup

6.1.1 Dichloromethane, "Distilled in Glass" or equivalent, stored in original containers and used as received.

6.1.2 Hexane, "Distilled in Glass" or equivalent, stored in original containers and used as received.

6.1.3 Acetone, "Distilled in Glass" or equivalent, stored in original containers and used as received.

6.1.4 Hydrochloric acid solution (6N). Slowly add 100 ml of HCl (12N) to 100 ml of reagent water.

6.1.5 Sodium hydroxide solution (6N). Dissolve 24 g NaOH in reagent water and dilute to 100 ml.

6.1.6 Sodium sulfate (Na_2SO_4), Anhydrous, granular. Clean by overnight Soxhlet extraction with dichloromethane, drying in an oven at 110 to 160°C oven, and then heating to 650°C for 2 hr. Store in a glass jar tightly sealed with TFE-lined screw cap.

6.1.7 Silica gel, 75/150 mesh. Clean silica gel for 16 h by Soxhlet extraction with dichloromethane. Dry and activate for 16 h at 160°C. Deactivate by adding 3% water (by weight) and mixing for at least 4 h on a tumbler. Store at room temperature in glass jars fitted with TFE lined screw caps.

6.1.8 Florisil 60/100 mesh, Floridan. Clean florisil for 16 hr by Soxhlet extraction with dichloromethane. Dry and activate for 16 h at 160°C. Deactivate by adding 1% water by weight and mixing for at least 4 h on a tumbler. Store at room temperature in glass jars fitted with TFE lined screw caps.

6.1.9 Glass wool. Clean glass wool by thorough rinsing with hexane, dried in a 100°C oven, and stored in a hexane rinsed glass jar with TFE lined screw cap.

6.1.10 Boiling chips - silica or carborundum.

6.1.11 GPC Calibration Solutions

6.1.11.1 Corn oil, 200 mg/ml in dichloromethane.

6.1.11.2 Pentachlorophenol and di-n-octylphthalate, 4 mg/ml each in dichloromethane.

6.2 For Identification and Quantitation

6.2.1 Analytical Standards

6.2.1.1 Prepare stock solutions from the pure compounds by dissolving 10 mg quantities into 10 ml of dichloromethane. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

6.2.1.2 Transfer the stock standard solutions into TFE sealed screw cap bottles. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Quality control check standards are available from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, that can be used to determine the accuracy of calibration standards.

6.2.1.3 Stock standard solutions must be replaced after 6 months, or sooner if comparison with check standards indicate a problem.

6.2.1.4 Prepare mixed analytical standards by diluting aliquots of the stock solutions. The acids standard should contain each of the phenolic compounds at concentrations in the range of 50 to 200 ng/µl. The base, neutral, and pesticide (B/N/P) standard should be prepared at concentrations in the range of 20-100 ng/µl. All working standards must include d_{10}-anthracene at 20 ng/µl.

6.2.2 Analyte Spiking Solutions

Prepare mixed spiking solutions by serial dilution from the individual stock solutions prepared as described in Section 6.2.1. The specifications for spiking solutions for individual samples are described in Section 8.3.2.

6.2.3 Internal Standard Spiking Solution

Prepare d_{10}-anthracene internal spiking solutions at 20 µg/liter in dichloromethane as described in Section 6.2

6.2.4 Surrogate Standard Spiking Solution

Select a minimum of five B/N and two acid surrogate compounds from Table 2. Prepare and store stock standard and spiking solutions as described in Section 6.2.1.

6.2.5 DFTPP Standard

Prepare a 25 ng/µl solution of DFTPP in dichloromethane.

7. Method Calibration

7.1 Establish GC/MS operating parameters equivalent to those indicated in Section 12. The GC/MS system can be calibrated using the external standard technique or the internal standard technique.

7.2 External Standard Calibration Procedure

7.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with dichloromethane. One of the external standards should be at a concentration near, but above, the method detection limit and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.2.2 Using injections of 1 to 2 μl of each calibration standard, tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to amount injected in the calibration factor is a constant over the working range (< 10% relative standard deviation RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.2.3 Verify the working calibration curve or calibration factor on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ± 10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor must be prepared for that compound.

7.3 Internal Standard Calibration Procedure. To use this approach, select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. The internal standards used for this procedure must include d_{10}-anthracene.

7.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards and dilute to volume with dichloromethane. One of the standards should be at a concentration near, but above, the method detection limit, and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.3.2 Using injections of 2 to 5 µl of each calibration standard, tabulate peak height or area responses against concentration for each compound and internal standard, and calculate relative response factors (RRF) for each compound using Equation 1.

$$RRF = (A_s B_{is})/(A_{is} B_s) \qquad \text{(Eq. 1)}$$

where A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

B_{is} = Mass of the internal standard (ng).

B_s = Mass of the parameter to be measured (ng).

If the RRF value over the working range is a constant (< 10% RSD), the RRF can be assumed to be nonvariant and the average RRF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} vs. RRF.

7.3.3 Verify the working calibration curve or RRF on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ± 10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

7.4 Daily Calibration of the GC/MS System

7.4.1 At the beginning of each day, check the calibration of the GC/MS system and adjust if necessary to meet decafluorotriphenylphosphine (DFTPP) specifications (Section 7.4.3). Each day base/neutrals are measured, the column performance specification (Section 12) with benzidine must be met. Each day the acids are measured, the column performance specification (Section 12) with pentachlorophenol must be met. DFTPP can be mixed in solution with either of these compounds to complete two specifications with one injection, if desired.

7.4.2 To perform the calibration test of the GC/MS system, the following instrumental parameters are required.

Electron energy, 70 eV (nominal)

Mass range, m/e 40-475

Scan time to provide at least 5 scans per peak. Typical scan times are 3 s or less for acids or base/neutrals with the packed column, 1 s or less for base/neutrals with the capillary column.

7.4.3 Evaluate the system performance each day that it is to be used for the analysis of samples or blanks by examining the mass spectrum of DFTPP. Inject a solution containing 50 ng DFTPP and check to ensure that performance criteria listed in Table 3 are met. If the system performance criteria are not met, the analyst must retune the spectrometer and repeat the performance check. The performance criteria must be met before any samples or standards may be analyzed.

7.4.4 At the beginning of each working day, verify the calibration of the GC/MS system by injecting a standard mixture (Section 7.3.3).

7.4.5 For instrument performance verification, to each acid and base/neutral extract and each standard analyzed, add an amount of d_{10}-anthracene immediately prior to injection such that 40 ± 4 ng will be injected.

8. Quality Control

8.1 Demonstrate Acceptable Performance

Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this procedure.

8.1.1 For each compound to be measured, select a spike concentration representative of the expected levels in the samples. Using stock standards, prepare a quality control check standard in acetone 1,000 times more concentrated than the selected concentrations.

8.1.2 Add 80 µl of the check standard to each of a minimum of four 80 ml aliquots of reagent water with a syringe. A representative sludge can be used in place of the reagent water, but one or more additional aliquots must be analyzed to determine background levels, and the spike level must exceed twice the background level for the test to be valid. Analyze the aliquots according to the method beginning in Section 10.

8.1.3 Calculate average recovery (R) and standard deviation (s), in percentage recovery, for the results. Sludge background corrections must be made before R and s calculations are performed.

8.1.4 Using the appropriate data from Tables 12-14, determine the recovery and single operator precision expected for the method for each parameter, and compare these results to the values calculated in Section 8.1.3. If the data are not comparable, the analyst must review potential problem areas and repeat the test.

8.2 Precision and Accuracy Statement. The analyst must calculate method performance criteria for each of the surrogate standards.

8.2.1 Calculate upper and lower control limits for method performane for each surrogate standard, using the values for R and s calculated in Section 8.1.3:

$$\text{Upper Control Limit (UCL)} = R + 3\ s$$
$$\text{Lower Control Limit (LCL)} = R - 3\ s$$

The UCL and LCL can be used to construct control charts[4] that are useful in observing trends in performance.

8.2.2 For each surrogate standard, the laboratory must develop and maintain separate accuracy statements of laboratory performance for wastewater samples. An accuracy statement for the method is defined as R ± s. The accuracy statement should be developed by the analysis of four aliquots of sludge as described in Section 8.1.2, followed by the calculation of R and s. Alternately, the analyst must use four sludge data points gathered through the requirement for continuing quality control in Section 8.4. The accuracy statements should be updated regularly.[4]

8.3 Surrogate Spikes. The laboratory is required to spike all of their samples with the surrogate standard spiking solution to monitor spike recoveries. Suggested surrogate compounds are listed in Table 5. If the recovery for any surrogate standard does not fall within the control limits for method performance, the results reported for that sample must be qualified as described in Section 14.3. The laboratory should monitor the frequency of suspect data to ensure that it remains at or below 5%.

8.4 Method Blank. Before processing any samples, the analyst should demonstrate through the analysis of an 80 ml aliquot of reagent water, that all glassware and reagents are interference free. Each time a set of samples is extracted or there is a change in reagents, a laboratory reagent blank should be processed as a safeguard against laboratory contamination.

8.5 Fortified and Replicate Samples

8.5.1 Sample Selection. Select at least 30% of all samples or at least one sample from each sampling location for fortified and replicate aliquot analysis. Analyze the selected samples in duplicate to determine unspiked analyte concentrations. Using the procedures described in Section 8.5.2, spike and analyze duplicate aliquots of the selected samples. Analyze a third unspiked aliquot of the selected samples on the same day that the corresponding spiked aliquots are analyzed.

8.5.2 Spiking Procedures. Spike an 80 ml aliquot of sludge with the representative semivolatile compounds listed in Table 4 and with other compounds identified in the sample, if available, at two times the observed concentration or at 10 times the lower limit of detection, whichever is greater. Prepare the spike as two acetone solutions with the acidic and neutral compounds in the first solution and the basic compounds in the second solution. The concentrations of the spiking solutions should be such that 1 to 5 ml of each solution are added to the sludge sample to attain the required spike concentration. Homogenize the spiked sample for 45 to 60 s and store overnight at 4°C with tumbling before extraction and analysis.

9. Sampling and Preservation

9.1 Sampling. Collect samples in glass containers (1,000 to 4,000 ml) with a TFE lined screw cap. The container should be prewashed with acetone and dried before use. Containers should be filled no more than two-thirds full with sample to minimize breakage during freezing.

9.2 Preservation. Preferably, samples should be iced or refrigerated at 4°C for not more than 24 h before extraction. Where extraction cannot be performed within 24 h, samples should be frozen. Samples may be stored for up to 30 days at -20°C or indefinitely at -75°C. In order to prevent breakage during storage, the containers should not be slightly warmed and then recooled.

10. Sample Extraction

10.1 Preparation of Drying Column. Immediately prior to extracting a sample, prepare a drying tube for the extract. Place a small glass wool plug in the bottom of the column and add anhydrous sodium sulfate to a depth of 10 to 15 cm.

10.2 pH Adjustment. Thoroughly homogenize the sludge sample by mixing with an emulsifier in the sample bottle for 1 min, then quickly remove a 80 ml aliquot into a 250 ml graduated cylinder. Transfer the aliquot into a 250 ml centrifuge bottle. Basify to pH ≧ 11 with a 6 N sodium hydroxide solution. Mix briefly with the homogenizer to ensure uniform sample pH. (Note: If copious precipitation of carbonates is observed when sodium hydroxide is added, make the sample slightly acidic with 6 N hydrochloric acid and allow the carbon dioxide evolution to cease before basifying the sample.)

10.3 Basic Extraction. Add 80 ml of dichloromethane to the centrifuge bottle and homogenize for 45 to 60 s. Do not homogenize more than 60 s to avoid heating the sample. Cap the centrifuge bottles with TFE-lined screw caps and centrifuge at 2,500 to 3,000 rpm for 30 min. Stir and repeat centrifugation if satisfactory phase separation is not achieved. The mixture will separate into an aqueous layer over the dichloromethane extract with a solids cake at the water-dichloromethane interface. Withdraw the extract from each centrifuge bottle with a 100 ml syringe. Discharge the extracts into a 500 ml separatory funnel. Drain the dichloromethane through the drying column into a Kuderna-Danish evaporator. Retain any aqueous layer and return it to the centrifuge bottle. Extract the sample two more times to achieve three-fold extraction. Wash the drying column with an additional 100 ml of dichloromethane and combine the eluent with the dried extracts.

10.4 Extract Concentration. Add a boiling chip to the extract in the Kuderna-Danish evaporator and concentrate the extract to 8 ml using an 85°C bath or a steam bath. If the extract is only slightly colored and not notably viscous, fit a modified Snyder column onto the Kuderna-Danish receiving tube and immerse the tube halfway in a 35°C water bath. Direct a gentle stream of nitrogen directly on the surface of the extract until the volume is $\leqq$ 4 ml. Transfer the extract to a clean vial, seal it with TFE lined screw cap, and store the extract at 4°C. If the extract is highly colored, viscous or solidifies when concentrating to 4 ml, dilute the extract to 12 ml with dichloromethane, transfer to a clean vial, and store as described above.

10.5 Acidic Extraction. Acidify the sludge sample portions to pH $\leqq$ 2 with 6 N hydrochloric acid and extract the sample again by procedures described in Sections 10.3 to 10.4. Discard the extracted sludge aliquots.

11. Extract Cleanup

11.1 Base/Neutral Extracts. Clean the base/neutral sludge extracts by adsorption chromatography on either florisil or silica gel. Although there does not appear to be any significant difference in the performance of these adsorbents, the adsorbent selected for analyses of all quality assurance blanks, spiked blanks, and spiked sludges associated with a specific sludge sample must be the same as was selected for the original sample analysis. In cases where the base/neutral extracts are to be analyzed by packed column GC/MS, the GPC procedure (Section 11.2) may be used as an alternative cleanup method.

11.1.1 Column Preparation. Prepare a 200 mm x 20 mm ID silica gel or florisil column by pouring 20 g fresh 3% deactivated silica gel or fresh 1% deactivated florisil, into a chromatographic column containing 60 to 70 ml hexane. Tap the side of the clamped column with a stirring rod to aid packing and air bubble escape. If clumping should occur at the bottom of the solvent reservoir, a stirring rod can be used to break the clumps. Add hexane as needed. After most packing has settled, rinse down the florisil or silica gel adhering to the column walls with additional hexane. Wash the column with an additional 20 ml hexane until the solvent level is within 1 to 2 mm of the top of the silica gel or florisil.

11.1.2 Column Calibration.

11.1.2.1 Check the elution pattern for each new batch of adsorbent prepared by chromatographing a spiked blank. Mix 1 ml of a dichloromethane solution containing 100 µg of each of the specific analytes of interest and the representative B/N/P compounds included in quality assurance method spikes (described in Section 8.3) with 2 g of adsorbant. Evaporate the solvent with a gentle stream of dry nitrogen and add the adsorbant to the column.

11.1.2.2 Elute the column with 20 ml of hexane (Fraction I), 50 ml of 10% dichloromethane in hexane (Fraction II), 50 ml of 50% dichloromethane in hexane (Fraction III), and then 150 ml of 5% acetone in dichloromethane (Fraction IV). Maintain the elution flow at 2 to 4 ml/min.

11.1.2.3 Collect each fraction in separate Kuderna-Danish evaporators and concentrate the fractions according to the procedures described in Section 7.4.

11.1.2.4 Analyze each fraction by GC/FID or GC/MS with the SE-54 capillary or packed SP-2250 column. Determine the recovery of each compound in each fraction by comparing the detector responses with those from a duplicate aliquot of the original spiked blank. Elution patterns and recoveries observed for selected compounds chromatographed on silica gel and florisil are shown in Tables 5 and 6.

11.1.2.5 Increasing the volume of Fraction I may be required to provide acceptable cleanup for sludge extracts containing high concentrations of aliphatic hydrocarbons or other non-polar compounds. However, additional hexane may elute significant portions of the chlorinated benzenes, hexachloroethane, hexachlorobutadiene, hexachlorocyclopentadiene, 2-chloronaphthalene, aldrin, and p,p'-DDE. The elution patterns and recoveries observed for many B/N/P compounds chromatographed on silica gel using 100 ml of hexane for Fraction I are shown in Table 7. In cases where the volume of Fraction I must be increased to achieve acceptable cleanup and the analytes of interest include the compounds listed in this section, Fraction I must be analyzed separately from Fraction II-IV.

11.1.3 Column Operation.

11.1.3.1 Place 2 g of fresh 1% deactivated florisil or 3% deactivated silica gel into a small beaker and add the concentrated base/neutral extract. Dry the sample with a gentle nitrogen stream with stirring to ensure fast and uniform drying. Load dried florisil or silica gel containing the sludge components into the column. Elute the column as described in Section 11.1.2. Discard Fraction I.

11.1.3.2 Collect and composite in Kuderna-Danish evaporators all fractions containing the compounds of interest such as Fractions II through IV for all B/N/P compounds. Fraction II frequently contains much higher levels of interfering materials than to Fractions III or IV. As a result, it should not be composited with Fractions III and IV if it contains no compounds of interest. Fractions may be analyzed separately if desired.

11.1.3.3 Concentrate all fractions collected to 1 ml according to procedures described in Section 10.4.

11.2 Acidic Fraction. Gel permeation chromatography is used to remove triglycerides and fatty acids.

11.2.1 GPC Column Preparation. Place 70 g of Bio-Beads SX-3 in a 400 ml beaker. Cover the beads with dichloromethane and allow the beads to swell overnight before packing the columns. Transfer the swelled beads to the column and start pumping solvent, dichloromethane, through the column, with upward flow at 5.0 ml/min. After ∿ 1 h, adjust the pressure on the column to 350 to 700 millibars (5 to 10 psi) and pump an additional 4 h to remove air from the column. Adjust the column pressure periodically as required to maintain 350 to 700 millibars.

11.2.2 Column Calibration.

11.2.2.1 Calibrate the GPC column elution at least once a week according to the following procedure. Load 5 ml of the corn oil solution into sample loop No. 1 and 5 ml of the phthalate-phenol solution into loop No. 2. Inject the corn oil and collect 10 ml fractions, for 36 min, changing the fraction at 2 min intervals. Inject the phenols solution and collect 10-ml fractions for 1 h.

11.2.2.2 Determine the corn oil elution pattern by evaporation of each fraction to dryness followed by a gravimetric determination of the residue.

11.2.2.3 Analyze the phthalate-phenol fractions by GC/FID on the SP-2250 and SP-1240-DA columns. Plot the concentration of each component in each fraction versus total eluent volume (or time) from the injection points.

11.2.2.4 Choose a "dump time" which allows ≧ 85% removal of the corn oil and ≧ 85% recovery of the di-n-octylphthalate. Choose the "collect time" to extend at least 10 min after the elution of pentachlorophenol. "Wash" the column 20 min between samples. Typical parameters selected are: dump time, 20 min (100 ml); collect time, 30 min (150 ml); and wash time, 20 min (100 ml).

11.2.2.5 The column can also be calibrated using a 254-nm UV detector to monitor the elution of the corn oil and the phenols. Measure the peak areas at various elution times to determine appropriate fractions.

11.2.3 Column Operation.

11.2.3.1 Prefilter or load all extracts via the filter holder to avoid particulates that might cause flow stoppage. Load the ≦ 4-ml extracts into the 5-ml loops with a clean solvent on both sides of the extract. Load the ∿ 12-ml extracts in three consecutive loops. Use sufficient clean solvent after the extract to transfer the entire aliquot into the loop. Between extracts, purge the sample loading tubing thoroughly with clean solvent. After especially dirty extracts, run a GPC blank using dichloromethane to check for carry-over. Process the extracts using the dump, collect, and wash parameters determined from the calibration and collect the cleaned extracts in 250 ml brown bottles.

11.2.3.2 Concentrate the cleaned extracts, combining collected fractions from multiple injections, to ∿ 8 ml using Kuderna-Danish evaporators and then to ≦ 1 ml using modified Snyder columns and nitrogen blowdown.

11.2.3.3 Transfer the cleaned extracts to 8 ml graduated tubes and dilute to 4 ml with dichloromethane. Store at 4°C for GC/MS analysis. Intensely colored extracts may require a second GPC cleanup.

11.2.3.4 Note: Sample extracts must be in the same solvent used for column elution. Injection of solutions in other solvents can cause a significant change in the bead swell. In extreme cases a traumatic pressure increase may damage the column and cap, or even break the glass column.

12. Sample Extract Analysis

12.1 Base/Neutral/Pesticide Extracts. Analyze the B/N/P extracts by GC/MS using the capillary column or packed column systems described in Section 5.2.1 under the conditions shown below. The capillary column GC/MS procedure is preferred because this procedure provides more unambiguous interpretation of the resulting data. However, if satisfactory performance of the column cannot be demonstrated or if the required Grob-type injection system with direct capillary GC/MS interface is not available, the packed column GC/MS procedure may be used.

12.1.1 Capillary GC/MS with a SE-54 WCOT Column

12.1.1.1 Column Temperature: ~~50°C for~~ 4 min, 50 to 320°C at 4°C/min, and 320°C until after the elution time for benzo[g,h,i]perylene.

GC/MS interface, 300°C

Carrier gas helium at 10 psi

Splitless injection for 30 s

Injection size, 2 μl

Examples of the separations achieved by this column are shown in Figure 2. Relative retention times for the base/neutral compounds on this column are listed in Table 8.

12.1.1.2 Capillary Column GC/MS Performance Checks

12.1.1.2.1 Column Performance Screening. Fully evaluate the performance of each new column by GC/FID prior to installation in the GC/MS system.[5] In addition, recheck columns that show a marked decrease in performance on the GC/MS (as described in Section 12.2.1.3) or that have not been used the previous 2 weeks for GC/MS analyses under this protocol. Install the capillary column in a gas chromatograph equipped with a Grob-type split/splitless injector and flame ionization detector. Adjust carrier gas at about 15 to 20 cm/s for N_2

or 30 to 40 cm/s when He or hydrogen are used as the carrier gas. Set the splitter flow at 30 to 50 ml/min, makeup gas at 30 ml/min, and column oven temperature at 85°C. Using splitless injection, inject 2 µl of a column performance test mixture containing 20 ng each of 2,6-dimethylphenol, 2,6-dimethylaniline, 1-octanol, 2-octanone, n-tridecane, and n-tetradecane or an equivalent commercially available test mixture. Table 9 shows the contents of three appropriate commercial mixtures. Measure the pH of the column as the ratio of the peak height of 2,6-dimethylaniline to that of 2,6-dimethylphenol. A value of 0.5 to 1.5 is acceptable. Determine the activity of the column toward polar compounds by determining both the asymmetry for the 1-octanol peak and the ratio of the peak height of 1-octanol to that of C_{13} alkane. The peak asymmetry is evaluated by drawing a perpendicular from the apex of the peak to the baseline and measuring the width from the front of the peak to the perpendicular line (W_F) and from the back of the peak to the perpendicular line (W_B).

$$AS = \frac{W_B}{W_F} \times 100$$

Peak asymmetries between 75 and 200 are acceptable. The ratio of peak height of the 1-octanol to that of C_{13} alkane should be higher than 0.5. Determine the number of effective theoretical plates (N_{eff}) from the tridecane peak using the equation

$$N_{eff} = 5.545 \left(\frac{tr'}{W_{0.5}}\right)^2$$

where tr' is the adjusted retention time of tridecane and $W_{0.5}$ is the peak width at half height. The number of effective plates of acceptable columns must be at least 25,000.

12.1.1.2.2 System Performance. Evaluate the performance of the capillary column in the GC/MS system each time the column is installed and each working day prior to its use. Using splitless injection, inject 2 µl of a test mixture containing 20 ng each of 2,6-dimethylaniline, 2,6-dimethylphenol, methylstearate, octadecene, and octadecane. Measure the pH of the column by taking the ratio of peak heights of 2,6-dimethylaniline to that of 2,6-dimethylphenol. A pH of 0.5 to 1.5 is acceptable. Determine the resolution of the peaks corresponding to octadecane and octadecene. The peaks should be resolved with a 50% valley or better. Determine the asymmetry of the methylstearate peak according to the formula given in Section 12.1.1.2.a. If the methylstearate peak tails, the GC/MS transfer line is not adequately heated.

12.1.2 Packed Column GC/MS with a SP-2250 Column

Analyze B/N extracts by GC/MS using the SP-2250 column described in Section 5.2.1, operated under the following conditions.

Column temperature, 60°C for 2 min, 60 to 260°C at 80°C/min, and 260°C until after the elution time for benzo-[g,h,i]perylene.

Injector temperature, 225°C

GC/MS interface temperature, 275°C

Carrier gas, helium at 30 ml/min

Injection size, 2 µl

An example of the separation achieved by the column is shown in Figure 3. Relative retention times for the base/neutral and pesticide compounds on this column are listed in Table 10.

12.2 Acid Extracts

Analyze acid extracts by GC/MS using the SP-1240-DA column described in Section 5.2.1, operated under the following conditions.

Column temperature, 85°C for 2 min, 85 to 185°C at 10°C/min and 185°C until after the elution time for 4-nitrophenol.

Injector temperature, 185°C.

GC/MS surface temperature, 275°C.

Carrier gas, helium at 30 ml/min.

Injection size, 2 µl.

An example of the separation achieved by the column is shown in Figure 4. Relative retention times for the acid compounds are listed in Table 11.

13. Qualitative and Quantitative Determination

13.1 Using the characteristic mass spectral ions listed in Tables 8 or 10 for the base/neutral and pesticide compounds and in Table 11 for the acid compounds, plot at least three extracted ion current plots (EICPs) for each analyte.

13.2 Identify the presence of analytes by the coincidence of peaks in the characteristic EICPs at the appropriate retention times and with intensities in the characteristic ratios (Tables 8 or 10 and 11).

13.3 Record the area (intensity) of the peak in the EICP for the most intense ion for each compound identified.

14. Calculations

14.1 Determine the concentration of individual compounds in the sample.

14.1.1 If the external standard calibration procedure is used, calculate the amount of material injected from the peak response using the calibration curve or calibration factor in Section 7.2.2. The concentration in the sample can be calculated from Equation 2:

$$\text{Concentration, } \mu\text{g/liter} = \frac{(M)(V_e)}{(V_i)(V_s)} \qquad \text{(Eq. 2)}$$

where: M = Mass of material injected (ng).

V_i = Volume of extract injected (μl).

V_e = Volume of total extract (ml).

V_s = Volume of wet sludge extracted (liter)

14.1.2 If the internal standard calibration procedure was used, calculate the concentration in the sample using Equation 3.

$$\text{Concentration, } \mu\text{g/liter} = \frac{(A)(I_s)(V_e)}{(A_{is})(RRF)(V_i)(V_s)} \qquad \text{(Eq. 3)}$$

where: A = Area of peak in sample extract.

A_{is} = Area of internal standard peak in sample extract.

I_s = Areas of internal standard injected (ng).

V_e = Total volume of extract (ml).

V_i = Volume of extract injected (μl).

V_s = Volume of sludge extracted (liter).

RRF = Relative response factor.

14.2 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

14.3 If the surrogate standard recoverues fall outside the limits in Section 8.2, data for all parameters in that sample must be labeled as suspect.

15. Method Performance

Performance data for the application of this method to both POTW and industrial sludges are shown in Tables 12 to 14. Table 12 shows data for B/N compounds analyzed in POTW and industrial sludges via Option A, i.e., extract cleanup by silica gel chromatography and analysis by HRGC/MS. Table 13 shows data for B/N compounds analyzed via Option B, i.e., extract cleanup by GPC and analysis by packed column GC/MS, and acidic compounds in aliquots of the same sludges. Data for B/N compound were analyzed via Option B and acidic compounds in sludges from 40 POTWs. Most of these data represent results from one laboratory. Approximately 25% of the data in Table 14 was contributed by a second laboratory.

16. References

1. "Carcinogens - Working With Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

2. "OSHA Safety and Health Standards, General Industry" (29CFR1910), Occupational Safety and Health Administration, OSHA 2206 (Revised January 1979).

3. "Safety in Academic Chemistry Laboratories," American Chemical Society Committee on Chemical Safety, 3rd Edition Publication (1979).

4. "Handbook of Analytical Quality Control in Water and Wastewater Laboratories," EPA-600/4-79-019, U.S. Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1979.

5. Grob, K., Jr., G. Grob, and K. Grob, "Comprehensive Standardized Quality Test for Glass Capillary Columns," J. Chrom., 156, 1-20 (1978).

17. Additional Sources

1. "Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants." U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, March 1977, Revised April 1977. Effluent Guidelines Division, Washington, DC 20460.

2. "Methods 330.4 (Titrimetric, DPD-FAS) and 330.5 (Spectrophotometric, DPD) for Chlorine, Total Residual," Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory - Cincinnati, OH 45268. In preparation.

3. "Preservation and Maximum Holding Time for the Priority Pollutants," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268. In preparation.

4. Budde, W. L., and J. W. Eichelberger, "Performance Tests for the Evaluation of Computerized Gas Chromatography/Mass Spectrometry Equipment and Laboratories," EPA-600/4-80-025, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, p. 16, April 1980.

5. Kleopfer, R. D., "Priority Pollutant Methodology Quality Assurance Review," U.S. Environmental Protection Agency, Region VII, Kansas City, KS. Seminar for Analytical Methods for Priority Pollutants, Norfolk, VA, January 17-18, 1980, U.S. Environmental Protection Agency, Office of Water Programs, Effluent Guidelines Division, Washington, DC 20460.

TABLE 1. EXTRACTABLE ORGANIC PRIORITY POLLUTANTS

Compound	CAS No.
Acids	
2-Nitrophenol	88-75-5
4-Nitrophenol	100-02-7
Pentachlorophenol	87-86-5
Phenol	108-95-2
2,4,5-Trichlorophenol	88-06-2
4-Chloro-3-methylphenol	59-50-7
2-Chlorophenol	95-57-8
2,4-Dichlorophenol	120-83-2
2,4-Dimethylphenol	105-67-9
4,6-Dinitro-2-methylphenol	534-32-1
Bases	
Benzidine	93-87-5
3,3'-Dichlorobenzidine	92-94-1
Polycyclic Aromatic Hydrocarbons	
Acenaphthene	83-32-9
Acenaphthylene	208-96-8
Anthracene	120-12-7
Benz[*a*]anthracene	56-55-3
Benzo[*b*]fluoranthene	205-99-2
Benzo[*k*]fluoranthene	207-08-9
Benzo[*g*,*h*,*i*]perylene	191-24-2
Benzo[*a*]pyrene	50-32-8
Chrysene	218-01-9
Dibenz[*a*,*h*]anthracene	53-70-3
Fluoranthene	206-44-0
Fluorene	86-73-7
Indeno[1,2,3-*cd*]pyrene	193-39-5
Naphthalene	91-20-3
Phenanthrene	85-01-8
Pyrene	129-00-0
Phthalates	
Bis(2-ethylhexyl)phthalate	117-81-7
Butylbenzylphthalate	85-68-7
Diethylphthalate	84-66-2
Dimethylphthalate	131-11-3
Di-*n*-butylphthalate	84-74-2
Di-*n*-octylphthalate	117-84-0

(continued)

TABLE 1 (continued)

Compound	CAS No.
Chlorinated Hydrocarbons	
2-Chloronaphthalene	91-58-7
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-7
Hexachlorobenzene	118-74-1
Hexachloro-1,3-butadiene	87-68-3
Hexachloroethane	67-72-1
Hexachlorocyclopentadiene	77-47-4
1,2,4-Trichlorobenzene	129-82-1
Chloroalkyl Ethers	
Bis(2-chloroethyl)ether	111-44-4
Bis(2-chloroethoxy)methane	111-91-1
Bis(2-chloroisopropyl)ether	39638-32-9
Miscellaneous Neutrals	
4-Bromophenyl phenyl ether	101-55-3
4-Chlorophenyl phenyl ether	7005-72-3
2,4-Dinitrotoluene	121-14-2
N-Nitrosodi-*n*-propylamine	621-64-7
N-Nitrosodimethylamine	62-75-9
2,6-Dinitrotoluene	606-20-2
Isophorone	78-59-1
Nitrobenzene	98-95-3
N-Nitrosodiphenylamine	86-30-6
1,2-Diphenylhydrazine	122-66-7
Pesticides	
β-Endosulfan	33213-65-9
α-BHC	319-84-6
γ-BHC	58-89-9
β-BHC	319-85-7
Aldrin	309-00-2
Heptachlor	76-44-8
Heptachlor epoxide	1024-57-3
α-Endosulfan	959-98-8
Dieldrin	60-57-1
4,4'-DDE	72-55-9
4,4'-DDD	72-54-8
4,4'-DDT	50-29-3

(continued)

TABLE 1 (concluded)

Compound	CAS No.
Endrin	72-20-8
Endosulfan sulfate	1031-07-8
δ-BHC	319-86-8
Chlordane	57-74-9
Toxaphene	8001-35-2
PCB-1242	53469-21-9
PCB-1221	11104-28-2
PCB-1254	11097-69-1
PCB-1232	11141-16-5
PCB-1248	12672-29-6
PCB-1260	11096-82-5
PCB-1016	12674-11-2

TABLE 2. SUGGESTED SURROGATE COMPOUNDS

Base/neutral fraction	Acid fraction
Aniline-d_5	2-Fluorophenol
Anthracene-d_{10}	Pentafluorophenol
Benzo[a]anthracene-d_{12}	Phenol-d_5
4,4'-Dibromobiphenyl	2-Perfluoromethyl phenol
4,4'-Dibromooctafluorobiphenyl	
Decafluorobiphenyl	
2,2'-Difluorobiphenyl	
2-Fluoraniline	
1-Fluoronaphthylene	
2-Fluoronaphthylene	
Naphthalene-d_8	
Nitrobenzene-d_5	
1,2,3,4,5-Pentafluorobiphenyl	
Pyridine-d_5	

TABLE 3. DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

m/e	Ion abundance criteria
51	30-60% of m/e 198
68	< 2% of m/e 69
70	< 2% of m/e 69
127	40-60% of 198
197	< 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of m/e 198
275	10-30% of m/e 198
365	1% of m/e 198
441	Present and < m/e 443
442	40% of m/e 198
443	17-23% of m/e 442

[a] Eichelberger, J. W., L. E. Harris, and W. L. Budde, "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry," Analytical Chemistry, 47, 995 (1975).

TABLE 4. REPRESENTATIVE EXTRACTABLE COMPOUNDS FOR RECOVERY STUDIES

Acenaphthylene
Benzidine
Benzo[*a*]pyrene
Bis(2-chloroethyl) ether
Bis(2-chloroisopropyl) ether
Bis(2-ethylhexyl)phthalate
Butylbenzyl phthalate
3,3'-Dichlorobenzidine
2,4-Dichlorophenol
2,4-Dimethylphenol
2,6-Dinitrotoluene
Fluoranthene
Hexachloroethane
N-Nitrosodimethylamine
1,4-Dichlorobenzene
Pentachlorophenol
Phenol
Dieldrin
α-BHC
p,*p*'-DDE
Heptachlor

TABLE 5. ELUTION PATTERNS AND RECOVERIES OF SELECTED BASE/NEUTRALS CHROMATOGRAPHED ON SILICA GEL[a]

Compound	Spike level (µg)	Fraction I hexane (20 ml)	Fraction II 10% dichloromethane/ hexane (50 ml)	Fraction III 50% dichloromethane/ hexane (50 ml)	Fraction IV 5% acetone/ dichloromethane (150 ml)	Total Recovery[b] (%)
1,4-Dichlorobenzene	46.8		+[c]	+		70
Hexachloroethane	31.2		+			83
Bis(2-chloroisopropyl)ether)	49.6				+	85
Bis(2-chloroethyl)ether	31.6				+	93
Acenaphthylene	28.5			+		79
2,6-Dinitrotoluene	35.1				+	96
Fluoranthene	27.0			+		90
3,3'-Dichlorobenzidine	36.4				+	50
n-Butylbenzylphthalate	45.2				+	97
Bis(2-ethylhexyl)phthalate	39.6				+	93
Benzo[a]pyrene	30.0			+		78

[a] 3% deactivated silica gel.

[b] Analyses done by packed column GC/MS.

[c] + indicates more than 1% recovery in that fraction.

TABLE 6. ELUTION PATTERNS AND RECOVERIES OF SELECTED BASE/NEUTRALS CHROMATOGRAPHED ON FLORISIL[a]

Compound	Spike level (μg)	Fraction I hexane (20 ml)	Fraction II 10% dichloromethane/ hexane (50 ml)	Fraction III 50% dichloromethane/ hexane (50 ml)	Fraction IV 5% acetone/ dichloromethane (150 ml)	Total Recovery[b] (%)
1,4-Dichlorobenzene	93.6		+[c]	+	+	48
Hexachloroethane	62.4		+	+	+	67
Bis(2-chloroisopropyl)ether	42.2			+	+	150
Bis(2-chloroethyl)ether	66.2			+	+	48
Acenaphthylene	57.0		+	+	+	92
2,6-Dinitrotoluene	70.2				+	130
Fluoranthene	54.0		+	+	+	120
3,3'-Dichlorobenzidine	72.8				+	65
n-Butylbenzylphthalate	90.4				+	110
Bis(2-ethylhexyl)phthalate	79.2				+	92
Benzo[a]pyrene	60.0			+	+	87

[a] 1% deactivated florisil.

[b] Analyses done by packed column GC/MS.

[c] + indicates more than 1% recovery in that fraction.

TABLE 7. ELUTION PATTERNS AND RECOVERIES OF SELECTED BASE/NEUTRAL/PESTICIDES CHROMATOGRAPHED ON SILICA GEL WITH AN ALTERNATE ELUTION[a,b] SCHEME

Compound	Fraction I hexane (100 ml)	Fraction II 10% dichloromethane/ hexane (50 ml)	Fraction III 50% dichloromethane/ hexane (50 ml)	Fraction IV 5% acetone/ dichloromethane (150 ml)	Total Recovery[c] (%)
Bis(2-chloroethyl)ether				+[d]	95 ± 22
1,3-Dichlorobenzene	+				64 ± 6
1,2-Dichlorobenzene	+				67 ± 9
Hexachloroethane	+				73 ± 14
N-nitrosodi-n-propylamine				+	94 ± 12
Nitrobenzene			+	+	67 ± 3
Bis(2-chloroethoxy)methane				+	66 ± 5
1,2,4-Trichlorobenzene	+				70 ± 17
Naphthalene	+	+	+		58 ± 7
Hexachlorobutadiene	+				140 ± 51
Hexachlorocyclopentadiene	+				300 ± 55
2-Chloronaphthalene	+	+			94 ± 5
Acenaphthylene		+	+		77 ± 21
2,6-Dinitrotoluene				+	93 ± 19
Acenaphthalene		+	+		88 ± 12
2,4-Dinitrotoluene				+	95 ± 14
Fluorene			+		87 ± 22
4-Chlorophenylphenylether			+		110 ± 12
Diethylphthalate				+	90 ± 41
4-Bromophenylphenylether			+		120 ± 15
Hexachlorobenzene	+				85 ± 30
Phenanthrene			+		85 ± 30
Anthracene			+		83 ± 28

(continued)

TABLE 7 (continued)

Compound	Fraction I hexane (100 ml)	Fraction II 10% dichloromethane/ hexane (50 ml)	Fraction III 50% dichloromethane/ hexane (50 ml)	Fraction IV 5% acetone/ dichloromethane (150 ml)	Total Recovery[c] (%)
Di-n-butylphthalate				+	80 ± 51
Fluoranthene			+		51 ± 20
Pyrene			+		63 ± 12
Endosulfan sulfate				+	67 ± 17
n-Butylbenzylphthalate				+	87 ± 35
Chrysene			+		72 ± 5
3,3'-Dichlorobenzidine				+	40 ± 2
Bis(2-ethylhexyl)phthalate				+	95 ± 61
Benzo[a]pyrene			+		70 ± 34
Dibenz[a,h]anthracene			+		84 ± 17
γ-BHC		+	+	+	66 ± 27
Aldrin	+				67 ± 14
Heptachlorepoxide			+	+	88 ± 3
p,p'-DDE	+	+	+		80 ± 6
Endrin				+	77 ± 18
p,p'-DDD			+		78 ± 7
p,p'-DDT			+	+	91 ± 17
α-Endosulfan			+	+	86 ± 17

a Data from Lopez-Avila, Viorica, Raymond V. Northcutt, Jon Onstot, and Margie Wickham. "Analysis of the NBS Sediment by the MRI Sludge Protocol," Final Report prepared for the Environmental Protection Agency under EPA Contract No. 68-03-2711 (1981).

b 3% reactivated silica gel.

c Recoveries determined in duplicate at 8-μg and 80-μg levels for each compound. Analyses done by fused silica capillary GC/MS.

d + indicates more than 1% recovery in that fraction.

TABLE 8. CHROMATOGRAPHIC CONDITIONS AND CHARACTERISTIC EI IONS FOR THE BASE/NEUTRAL COMPOUND ANALYZED BY CAPILLARY COLUMN GC/MS

Compound	RRT[a,b]	Characteristic EI ions (relative intensity)
N-Nitrosodimethylamine	0.04	42(100), 74(88), 44(21)
Bis(2-chloroethyl)ether	0.21	93(100), 63(99), 95(31)
1,3-Dichlorobenzene	0.22	146(100), 148(64), 113(12)
1,4-Dichlorobenzene	0.22	146(100), 148(64), 113(11)
1,2-Dichlorobenzene	0.25	146(100), 148(64), 113 (11)
Bis(2-chloroisopropyl)ether	0.29	45(100), 77(19), 79(12)
Hexachloroethane	0.29	117(100, 199(61), 201(99)
N-Nitrosodi-n-propylamine	0.31	130(22), 42(64), 101(12)
Nitrobenzene	0.32	77(100), 123(50), 65(15)
Isophorone	0.36	82(100), 95(14), 138(18)
Bis(2-chloroethoxy)methane	0.41	93(100), 95(32), 123(21)
1,2,4-Trichlorobenzene	0.42	74(100), 109(80), 145(52)
Naphthalene	0.43	128(100), 223(63), 227(65)
Hexachlorobutadiene	0.47	225(100), 223(63), 227(65)
Hexachlorocyclopentadiene	0.60	237(100), 235(63), 272(12)
2-Chloronaphthalene	0.63	162(100), 164(32), 127(31)
Acenaphthylene	0.70	152(100), 153(16), 151(17)
Dimethylphthalate	0.72	163(100), 164(10), 194(11)
2,6-Dinitrotoluene	0.72	165(100), 63(72), 121(23)
Acenaphthene	0.73	154(100), 155(95), 152(13)
2,4-Dinitrotoluene	0.78	165(100), 63(72), 121(23)
Fluorene	0.82	166(100), 165(80), 167(14)
4-Chlorophenyl phenyl ether	0.84	204(100), 206(34), 141(29)
Diethylphthalate	0.84	149(100), 178(25), 150(10)
N-Nitrosodiphenylamine[c]	0.84	169(100), 168(71), 167(50)
1,2-Diphenylhydrazine[d]	0.86	77(100), 93(58), 105(28)
4-Bromophenyl phenyl ether	0.92	248(100), 250(99), 141(45)
Hexachlorobenzene	0.93	284(100), 142(30), 249(24)
Phenanthrene	0.98	178(100), 179(16), 176(15)
Anthracene	0.99	178(100), 179(16), 176(15)
d_{10}-Anthracene	1.00	188(100), 94(19), 80(18)
Di-n-butylphthalate	1.14	149(100), 150(27), 104(10)
Fluoranthene	1.19	202(100), 101(23), 100(14)
Pyrene	1.23	202(100), 101(26), 100(17)
Benzidene	1.24	184(100), 92(24), 185(13)
Butylbenzylphthalate	1.40	149(100), 91(50)
Chrysene	1.45	228(100), 229(19), 226(23)
3,3'-Dichlorobenzidene	1.47	252(100), 254(66), 126(16)
Bis(2-ethylhexyl)phthalate	1.52	149(100), 167(31), 279(26)
Benzo[k]fluoranthene	1.62	252(100), 253(23), 125(16)

(continued)

TABLE 8 (continued)

Compound	RRT[a,b]	Characteristic EI ions (relative intensity)
Di-n-octylphthalate	1.63	149(100), 167(29), 279(22)
Benzo[a]pyrene	1.67	252(100), 253(23), 125(21)
Dibenz[a,h]anthracene	1.84	278(100), 139(31), 279(12)
Benzo[g,h,i]perylene	1.87	276(100), 138(37), 277(25)

a Relative to d_{10}-anthracene. Retention times data were not determined for the priority pollutant pesticides and a few base/neutral compounds. However, their retention properties should be roughly equivalent to those on SP-2250 (see Table 6).

b SE-54 WCOT glass capillary (15 m x 0.24 mm ID), He at 10 psi, program: 50°C for 4 min, then 4°C/min to 320°C.

c Elutes as diphenylamine.

d Elutes as azobenzene.

TABLE 9. COMPOSITION OF CAPILLARY COLUMN PERFORMANCE TEST MIXTURES

Test mixture	Composition	
Varian P/N 82-005049-01 (nonpolar)	2-octanone	0.2 µg/µl
	1-octanol	0.2
	naphthalene	0.2
	2,6-dimethylphenol	0.2
	2,4-dimethylaniline	0.2
	C_{12}-alkane	0.2
	C_{13}-alkane	0.2
Alltech TP-5 (polar)	C_{13}-alkane	0.1 µg/µl
	C_{14}-alkane	0.1
	C_{15}-alkane	0.1
	C_{16}-alkane	0.1
	1-octanol	0.5
	5-nonanone	0.3
	2,6-dimethylaniline	0.4
	2,6-dimethylphenol	0.4
	naphthalene	0.5
Analabs Test probe LPK-013F (general purpose)	C_{12}-acid methyl ester	41 ng/µl
	C_{11}-acid methyl ester	41
	C_{10}-acid methyl ester	42
	C_{10}-alkane	28
	C_{11}-alkane	29
	1-octanol	36
	Nonanal	40
	2,3-butanediol	53
	2,6-dimethylphenol	32
	2,6-dimethylaniline	32
	dicyclohexylamine	31
	2-ethylhexanoic acid	38

TABLE 10. CHROMATOGRAPHIC CONDITIONS AND CHARACTERISTIC IONS FOR THE BASE/NEUTRAL AND PESTICIDE COMPOUNDS ANALYZED BY PACKED COLUMN GC/MS

Compound	RRT[a,b]	Characteristic EI ions (relative intensity)
N-Nitrosodimethylamine	0.15	42(100), 74(88), 44(21)
1,3-Dichlorobenzene	0.31	146(100), 148(64), 113(12)
1,4-Dichlorobenzene	0.33	146(100), 148(64), 113(11)
Hexachloroethane	0.35	117(100), 199(61), 201(99)
1,2-Dichlorobenzene	0.35	146(100), 140(64), 113(11)
Bis(2-chloroisopropyl)ether	0.37	45(100), 77(19), 79(12)
N-Nitrosodi-n-propylamine	0.42	130(22), 42(64), 101(12)
Nitrobenzene	0.45	77(100), 123(50), 65(15)
Isophorone	0.47	82(100), 95(14), 138(18)
Hexachlorobutadiene	0.48	225(100), 223(63), 227(65)
1,2,4-Trichlorobenzene	0.49	74(100), 109(80), 145(52)
Bis(2-chloroethoxy)methane	0.50	93(100), 95(32), 123(21)
Naphthalene	0.51	128(100), 127(10), 129(11)
Bis(2-chloroethyl)ether	0.55	93(100), 63(99), 95(31)
Hexachlorocyclopentadiene	0.60	237(100), 235(63), 272(12)
2-Chloronaphthalene	0.68	162(100), 164(32), 127(31)
Acenaphthylene	0.75	152(100), 153(16), 151(17)
Acenaphthene	0.77	154(100), 153(95), 152(53)
Dimethyl phthalate	0.78	163(100), 164(10), 194(11)
2,6-Dinitrotoluene	0.81	165(100), 63(72), 121(23)
Fluorene	0.85	166(100), 165(80), 167(14)
2,4-Dinitrotoluene	0.85	165(100), 63(72), 121(23)
4-Chlorophenyl phenyl ether	0.85	204(100), 206(34), 141(29)
Diethyl phthalate	0.87	149(100), 178(25), 150(10)
1,2-Diphenylhydrazine[b]	0.88	77(100), 93(58), 105(28)
N-Nitrosodiphenylamine[c]	0.89	169(100), 168(71), 167(50)
Hexachlorobenzene	0.92	284(100), 142(30), 249(24)
4-Bromophenyl phenyl ether	0.92	248(100), 250(99), 141(45)
Phenanthrene	0.99	178(100), 179(16), 176(15)
Anthracene	0.99	178(100), 179(16), 176(15)
Deuterated anthracene (D-10)	1.00	188(100), 94(19), 80(18)
D-n-butylphthalate	1.09	149(100), 150(27), 104(10)
Fluoranthene	1.18	202(100), 101(23), 100(14)
Pyrene	1.22	202(100), 101(26), 100(17)
Benzidine	1.27	184(100), 92(24), 185(13)
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin	1.33	322(100), 320(90), 59(95)
Butylbenzylphthalate	1.34	149(100), 91(50)
Bis(2-ethylhexyl)phthalate	1.37	149(100), 167(31), 279(26)
Chrysene	1.40	228(100), 229(19), 226(23)

(continued)

TABLE 10 (continued)

Compound	RRT[a,b]	Characteristic EI ions (relative intensity)
Benz[a]anthracene	1.40	228(100), 229(19), 226(19)
Benzo[b]fluoranthene	1.43	252(100), 253(23), 125(15)
Benzo[k]fluoranthene	1.43	252(100), 253(23), 125(16)
3,3'-Dichlorobenzidine	1.45	252(100), 254(66), 126(16)
Di-n-octylphthalate	1.50	149(100), 167, 279
Benzo[a]pyrene	1.50	252(100), 253(23), 125(21)
Indeno[1,2,3-cd]pyrene	1.86	276(100), 138(28), 277(27)
Benzo[g,h,i]perylene	1.98	276(100), 138(37), 277(25)
Bis(chloromethyl) ether	d	45(100), 49(14), 51(5)
β-Endosulfan	0.47	201(100), 283(48), 278(30)
α-BHC	0.94	183(100), 109(86), 181(91)
γ-BHC	1.00	183(100), 109(86), 181(91)
β-BHC	1.03	181(100), 183(93), 109(62)
δ-BHC	1.04	183(100), 109(86), 181(90)
Aldrin	1.05	181(100), 183(93), 109(62)
Heptachlor	1.06	183(100), 109(86), 181(90)
Heptachlor epoxide	1.13	66(100), 220(11), 263(73)
α-Endosulfan	1.14	100(100), 353(79), 351(60)
Dieldrin	1.18	201(100), 283(48), 278(30)
4,4'-DDE	1.20	79(100), 263(28), 279(22)
4,4'-DDD	1.22	246(100), 248(64), 176(65)
4,4'-DDT	1.27	235(100), 237(76), 165(93)
Endrin	1.30	81(100), 82(61), 263(70)
Endosulfan sulfate	1.30	272(100), 387(75), 422(25)
Chlordane	1.05-1.26	373(19), 375(17), 377(10)[e]
Toxaphene	1.12-1.35	(231, 233, 235)[f]
PCB-1242	0.86-1.14	(224, 260, 294)[f]
PCB-1254	1.09-1.30	(294, 330, 362)[f]

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[a] 3% SP-2250 on 100/120 mesh Supelcoport in a 1.8 m x 2 mm ID glass column; He at 30 ml/min. Program: 60°C for 2 min, then 8°C/min to 260°C and hold for 15 min.

[b] Elutes as azobenzene.

[c] Elutes as diphenylamine.

[d] No data.

[e] These three ions are characteristic for the α and γ forms of chlordane. No stock should be set in these three for other isomers.

[f] These ions are listed without relative intensities since the mixtures they represent defy characterization by three masses.

TABLE 11. CHROMATOGRAPHIC CONDITIONS AND CHARACTERISTIC IONS FOR THE ACID COMPOUNDS ANALYZED BY PACKED COLUMN GC/MS

Compound	RRT[a,b]	Characteristic EI ions (relative intensity)
Chlorophenol	0.51	128(100), 64(54), 130(31)
2-Nitrophenol	0.55	139(100), 65(35), 109(8)
Phenol	0.61	94(100), 65(17), 66(19)
2,4-Dimethylphenol	0.67	122(100), 107(90), 121(55)
2,4-Dichlorophenol	0.69	162(100), 164(50), 98(61)
2,4,6-Trichlorophenol	0.79	196(100), 198(92), 200(26)
4-Chloro-*m*-cresol	0.86	142(100), 107(80), 144(32)
2,4-Dinitrophenol	1.04	184(100), 63(59), 154(53)
4,6-Dinitro-*o*-cresol	1.04	198(100), 182(35), 77(28)
Pentachlorophenol	1.13	266(100), 264(62), 268(63)
4-Nitrophenol	1.63	65(100), 139(45), 109(72)

[a] Relative to d_{10}-anthracene.

[b] 1% SP-1240-DA on 100/120 Supelcoport in a 1.2 m x 2 mm ID glass column; He at 30 ml/min. Program: 85°C for 2 min, then 10°C/min to 185°C and hold for 5 min.

TABLE 12. ACCURACY AND PRECISION FOR BASE/NEUTRAL EXTRACTABLE ORGANICS ANALYZED VIA OPTION A (SILICA GEL CLEANUP, HRGC/MS DETERMINATION) IN THREE POTW AND TWO INDUSTRIAL SLUDGES

	Three POTW sludges						Two industrial sludges					
				Spike recovery						Spike recovery		
Compound	Determinations	Spike level (µg/L)		Mean (%)	Standard deviation	Mean RSD for Tripl. (%)	Determinations	Spike level (µg/L)		Mean (%)	Standard deviation	Mean RSD for Tripl. (%)
		Minimum	Maximum					Minimum	Maximum			
1,4-Dichlorobenzene	27	400	40,000	44	25	37	18	400	40,000	65	59	32
Hexachloroethane	25	400	40,000	24	17	33	18	400	40,000	55	65	55
Bis(2-chloroethyl)ether	27	400	40,000	110	77	54	16	400	40,000	80	44	20
Acenaphthylene	27	400	40,000	110	66	26	15	400	40,000	95	27	14
2,6-Dinitrotoluene	25	400	40,000	33	35	72	15	400	40,000	89	63	42
Fluoranthene	24	400	40,000	140	64	25	15	400	40,000	110	42	18
Benzidine	18	7,900	80,000	31	31	49	12	780	80,000	120	96	25
3,3'-Dichlorobenzidine	9	402	4,130	50	78	66	a	-	-	-	-	-
Butylbenzylphthalate	18	4,000	40,000	140	59	18	12	400	40,000	130	92	19
Di-n-octylphthalate	18	400	40,000	130	75	40	15	400	48,800	130	71	30
Benzo[a]pyrene	21	400	40,000	110	43	24	15	400	40,100	82	70	30

a This compound was not spiked into the industrial sludges.

TABLE 13. ACCURACY AND PRECISION FOR BASE/NEUTRAL EXTRACTABLE ORGANICS ANALYZED VIA OPTION B (GPC CLEANUP, GC/MS DETERMINATION AND ACIDIC EXTRACTABLE ORGANICS IN THREE POTW AND TWO INDUSTRIAL SLUDGES

	Three POTW sludges						Two industrial sludges					
				Spike recovery						Spike recovery		
Compound	Determinations	Spike level (µg/L)		Mean (%)	Standard deviation	Mean RSD for Tripl. (%)	Determinations	Spike level (µg/L)		Mean (%)	Standard deviation	Mean RSD for Tripl. (%)
		Minimum	Maximum					Minimum	Maximum			
1,4-Dichlorobenzene	27	40	41,600	69	28	16	15	400	40,000	75	16	9
Hexachloroethane	23	400	44,100	48	17	10	16	400	40,000	56	31	14
Bis(2-chloroethyl)ether	25	400	40,700	220	190	17	16	400	40,000	120	51	7
Acenaphthylene	21	400	40,000	65	26	9	18	400	40,000	110	47	12
2,6-Dinitrotoluene	14	4,000	40,000	50	31	10	12	4,000	40,000	100	35	10
Fluoranthene	24	400	40,000	51	27	14	15	400	40,000	91	22	8
Benzidine	14	4,870	80,000	79	59	8	16	800	70,000	77	41	10
3,3'-Dichlorobenzidine	13	415	4,130	69	40	11	3	4,000	4,000	110	13	13
Butylbenzylphthalate	18	4,500	40,000	130	120	7	12	400	40,000	69	15	9
Di-n-octylphthalate	28	4,000	40,000	98	77	13	12	400	48,800	81	73	10
Benzo[a]pyrene	16	400	40,600	120	94	13	16	400	40,000	66	47	7
Phenol	24	400	46,300	73	26	27	14	400	40,000	72	34	26
2,4-Dimethylphenol	26	400	41,100	58	62	37	12	400	40,000	110	64	23
2,4-Dichlorophenol	21	399	40,000	89	32	18	15	400	40,000	140	96	15
Pentachlorophenol	26	400	40,000	120	67	37	10	400	40,000	50	16	28

TABLE 14. ACCURACY AND PRECISION FOR BASE/NEUTRAL EXTRACTABLE ORGANICS ANALYZED VIA OPTION B (GPC CLEANUP, GC/MS DETERMINATIONS) AND ACIDIC EXTRACTABLE ORGANICS IN PRIMARY SLUDGES FROM 40 POTWs[a]

		Spike recovery[b]		
Compound	Determinations	Mean (%)	Standard Deviation	Mean Avg. Rel. Dev. for Dupl.
1,3-Dichlorobenzene	27	86	39	11
1,2-Dichlorobenzene	24	68	25	11
Nitrobenzene	13	49	28	17
Hexachlorobutadiene	27	71	22	7
Naphthalene	27	94	37	8
2-Chloronaphthalene	27	89	33	8
Acenaphthalene	24	79	27	8
2,6-Dinitrotoluene	23	59	38	15
Fluorene	27	94	34	10
N-Nitrosodiphenylamine	24	140	84	11
4-Bromophenylphenylether	27	80	27	5
Di-*n*-butylphthalate	26	79	43	9
Fluoranthene	26	85	40	9
Pyrene	27	90	47	8
Butylbenzylphthalate	26	95	64	11
Bis(2-ethylhexyl)phthalate	22	65	34	8
Benzo[*a*]pyrene	27	85	49	11
1,4-Dichlorobenzene	27	82	34	11
Hexachloroethane	21	49	25	21
Isophorone	27	51	27	15
1,2,4-Trichlorobenzene	27	83	32	9
Bis(2-chloroethoxy)methane	24	54	27	12
Hexachlorocyclopentadiene	20	0	0	0
Acenaphthylene	19	76	24	9
Dimethylphthalate	27	50	33	20
2,4-Dinitrotoluene	26	65	50	14
Diethylphthalate	27	65	35	12
Hexachlorobenzene	27	63	21	10
Phenanthrene/anthracene	26	71	39	11
Chrysene/Benz[*a*]anthracene	27	71	27	11
Benzo[*g*,*h*,*i*]perylene	19	31	15	10
N-Nitrosodi-N-propylamine	24	77	54	13
1,2-Diphenylhydrazine	23	64	30	9
Benzidine	21	8	11	15
3,3'-Dichlorobenzidine	27	56	58	14
2-Chlorophenol	27	59	16	14
2-Nitrophenol	27	46	39	17
4-Nitrophenol	25	22	23	15
Phenol	26	66	28	11

(continued)

TABLE 14 (continued)

Compound	Determinations	Spike recovery[b]		
		Mean (%)	Standard Deviation	Mean Avg. Rel. Dev. for Dupl.
2,4-Dimethylphenol	27	34	39	20
2,4-Dichlorophenol	27	68	25	11
2,4,6-Trichlorophenol	27	71	25	13
1,3-Dichlorobenzene	27	86	39	11
p-Chloro-m-cresol	22	58	32	9
2,4-Dinitrophenol	24	14	27	11
4,6-Dinitro-o-cresol	26	13	24	15
Pentachlorophenol	27	84	43	15
α-BHC	27	39	32	10
Dieldrin	27	72	30	8
4,4'-DDE	27	57	19	11
Heptachlor	26	76	35	10

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[a] Swanson, Stephen E., T. Murry Williams, Lloyd M. Petrie, and Earl M. Hansen, "Survey of Analysis of POTW Sludges for Priority Pollutants: Part II Quality Assurance Data," Final Report prepared under EPA Contract No. 68-01-5915, Task 35 (1981).

[b] Minimum spike level 125 μg/L; maximum spike level 1,250 μg/L.

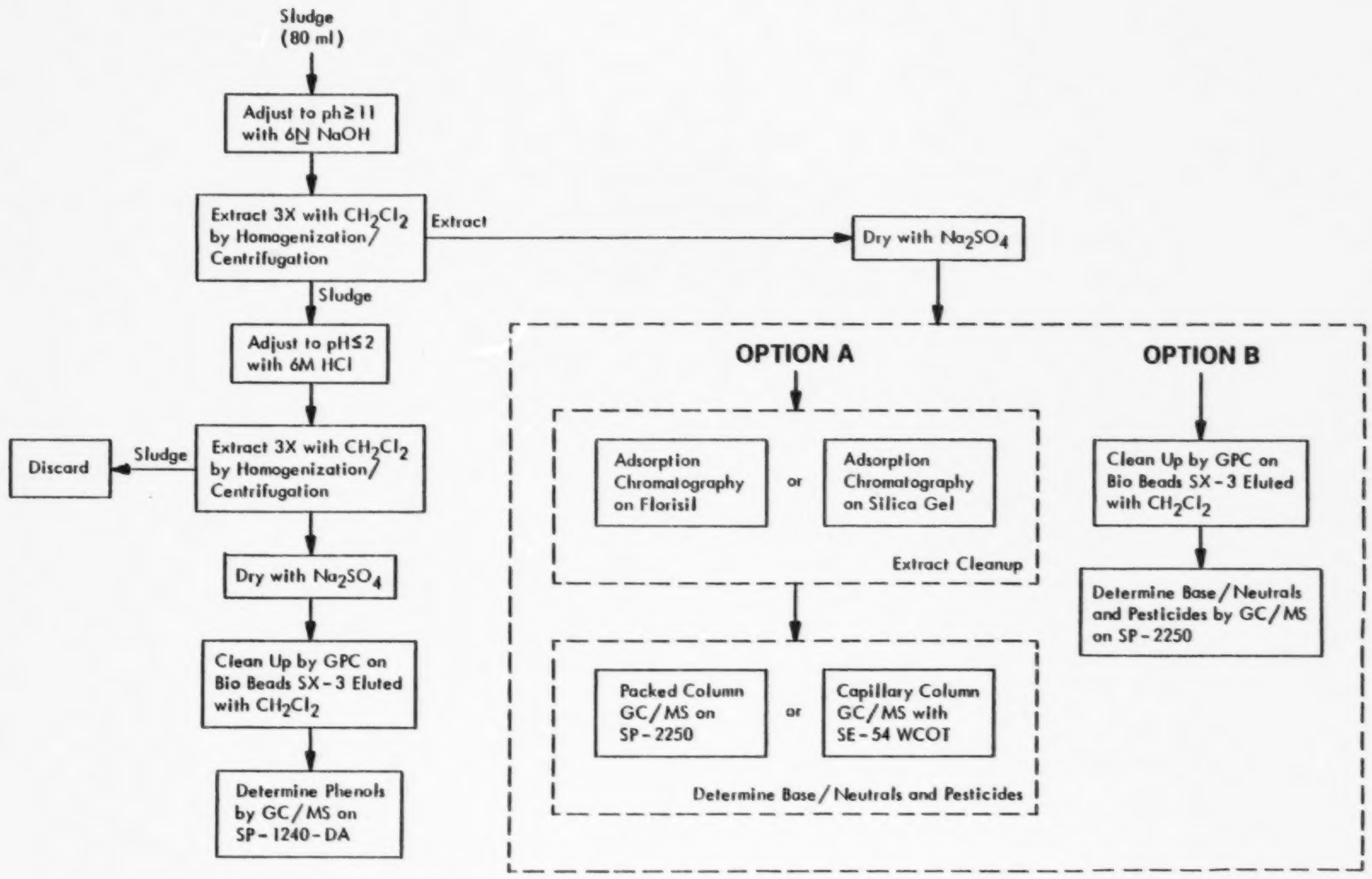
Sludge (80 ml)
Adjust to ph≥11 with 6N NaOH
Extract 3X with CH2Cl2 by Homogenization/Centrifugation
Extract
Dry with Na2SO4
Sludge
Adjust to pH≤2 with 6M HCl
Extract 3X with CH2Cl2 by Homogenization/Centrifugation
Sludge
Discard
Dry with Na2SO4
Clean Up by GPC on Bio Beads SX-3 Eluted with CH2Cl2
Determine Phenols by GC/MS on SP-1240-DA
OPTION A
Adsorption Chromatography on Florisil
or
Adsorption Chromatography on Silica Gel
Extract Cleanup
Packed Column GC/MS on SP-2250
or
Capillary Column GC/MS with SE-54 WCOT
Determine Base/Neutrals and Pesticides
OPTION B
Clean Up by GPC on Bio Beads SX-3 Eluted with CH2Cl2
Determine Base/Neutrals and Pesticides by GC/MS on SP-2250

Figure 1. Scheme for analysis of extractable organics in sludge.

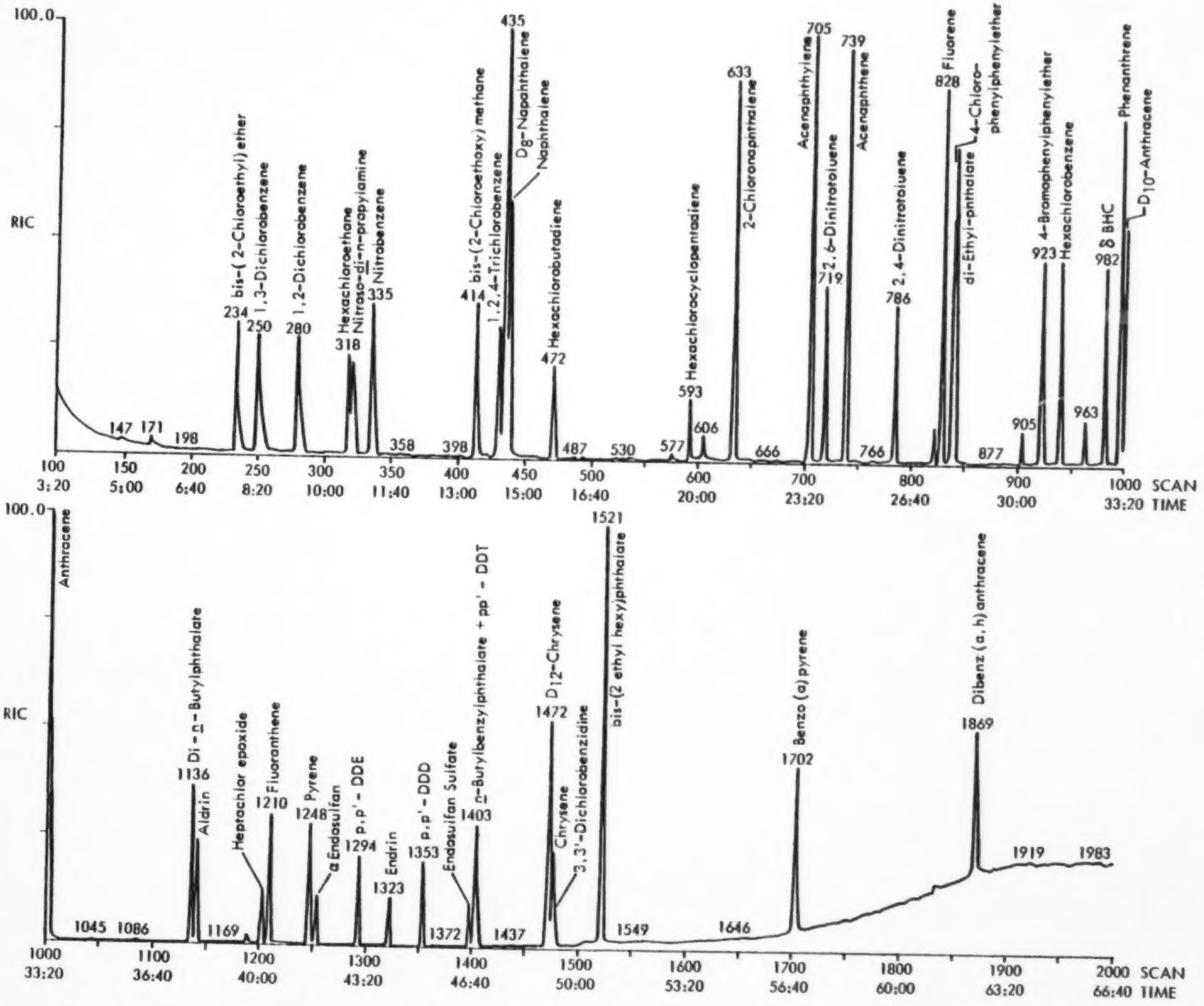

Figure 2. GC/MS chromatogram of base/neutral compounds on a fused silica capillary column.

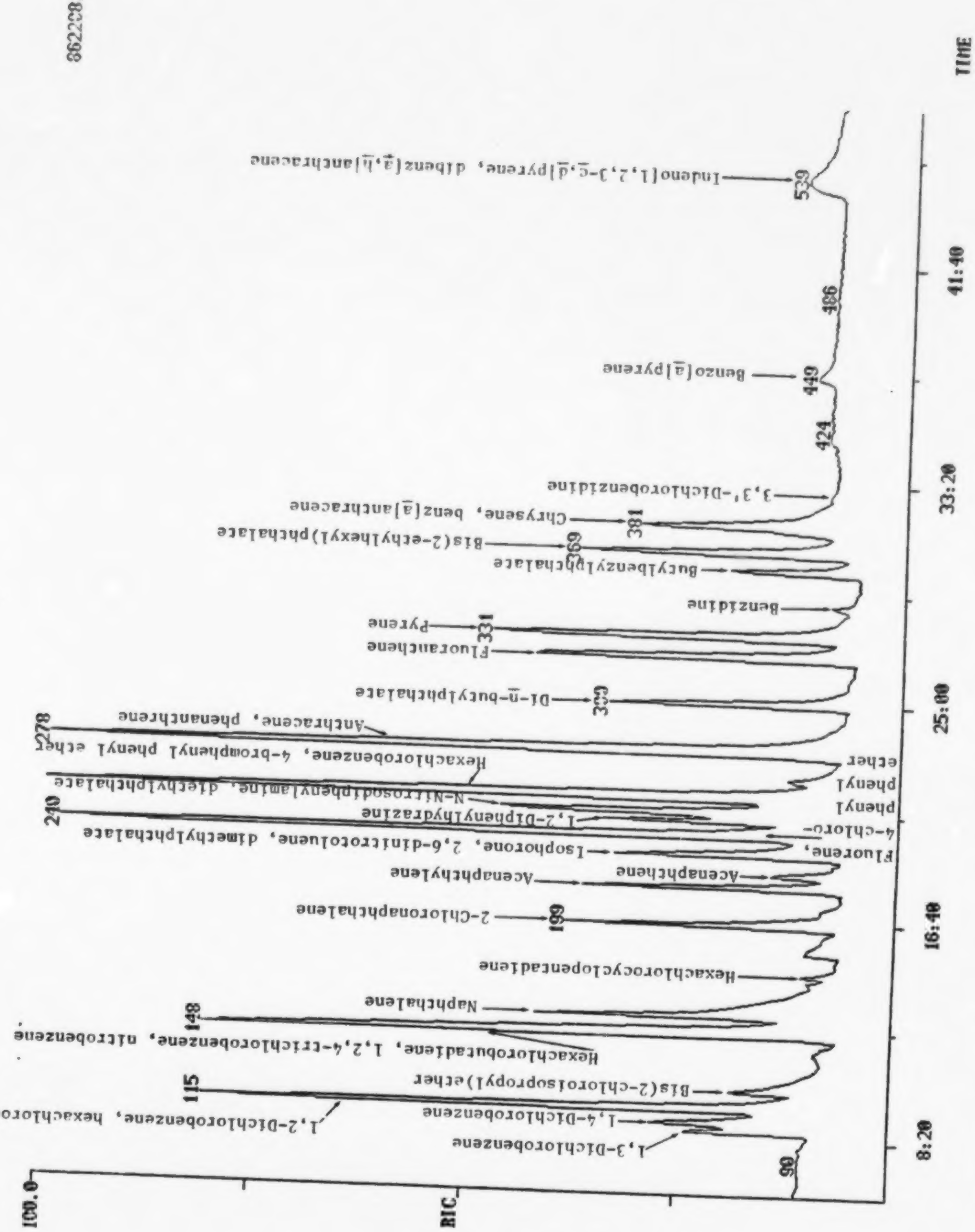

Figure 3. GC/MS chromatogram for the base/neutral compounds on a packed column.

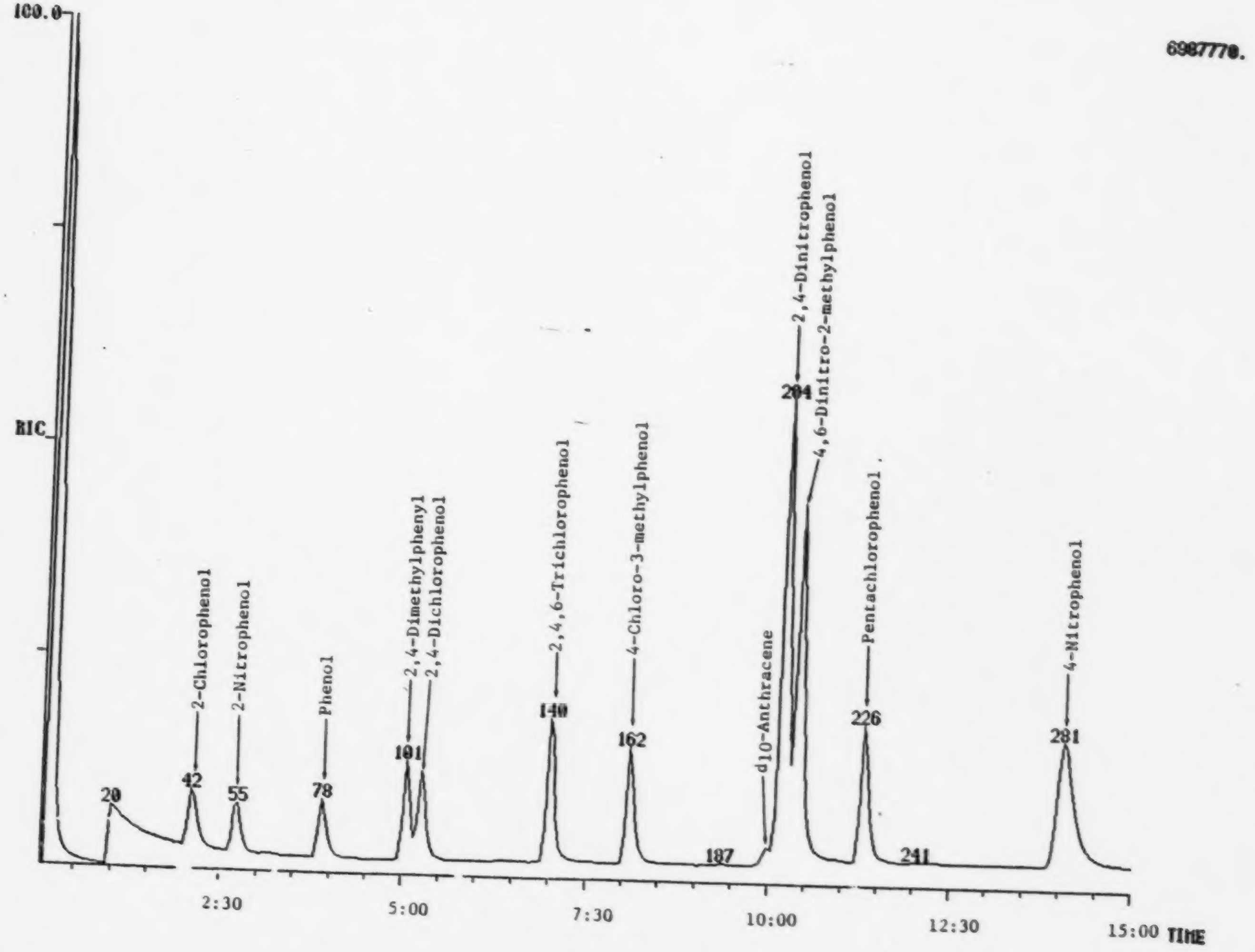

Figure 4. GC/MS chromatogram of the acidic compounds.